Heavy metal contamination of river water: sources, behaviour and remediation

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The candidate confirms that the work submitted is his/her own, except where work which has formed part of jointly authored publications has been included. The contribution of the candidate and the other authors to this work has been explicitly indicated below. The candidate confirms that appropriate credit has been given within the thesis where reference has been made to the work of others.

Chapter 2

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MVA (the candidate) collected the samples and prepared them for chemical and mineralogical analysis, conducted all of the data analysis, and made the figures and wrote the manuscript. RS, AS, RM helped with fieldwork including sample collection. AS provided training in how to use the geochemical model and output, and helped guide the analysis. AS and RM provided advice and guidance throughout and gave feedback on several drafts of the manuscript.

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MVA conducted the fieldwork, prepared the samples for chemical analyses, performed the data analysis, and prepared all the figures presented in the manuscript and wrote the manuscript. RS, and RM helped with fieldwork including sample collection. AS provided training in the application of the speciation model, helped guide the analysis and in the interpretations of outputs. All co-authors gave critical feedback on manuscript drafts.

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MVA developed the sampling strategy, prepared the instruments for fieldwork, prepared the samples for chemical analysis, performed the data analysis, and made all the figures presented in the manuscript and wrote the manuscript. RS helped with fieldwork including sample collection. AS and RM gave guidance on data interpretation and provided critical feedback on a draft of the manuscript.

Chapter 5

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MVA developed the sampling strategy, prepared the surveys, applied for ethical review, conducted the data analysis, and prepared the figures and wrote the manuscript. RS helped in scheduling field work dates, helped in the data collection including interviews and provided training in online survey tools. AS provided guidance and supervision throughout the writing process. AS and RM contributed with critical feedback on a draft of the manuscript.

Thesis by Alternative Format Rationale

This thesis is submitted as an alternative style of doctoral thesis including published material. This format is appropriate for this thesis because one out of the four data chapters has already been published in peer-reviewed journal, a second has positive reviews and an invitation to submit a revised manuscript and the third is currently in review. Loose copies of the published manuscript accompany this thesis. The fourth paper will be submitted in a peer reviewed journal after the thesis submission. The four manuscripts are preceded by an introduction (Chapter 1), including a review of the literature to give context to the work, an outline of the main research questions and the novelty of the research. A synthesis and conclusion section (Chapter 6) follows the research articles, and weaves together the findings of all four manuscripts, placing them in the context of the literature and the objectives, providing critical discussion and including directions for future work. This format follows the Faculty of Environment protocol for the format and presentation of an alternative style of doctoral thesis including published material.

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Abstract

Pollution from metal mining has led to severe environmental damage. The assessment of metals is very complex as they interact with a broad spectrum of biotic and abiotic components depending on physicochemical conditions. Worldwide, discharges from ancient mines are considered one of the major causes of point and diffuse pollution. This thesis investigated the sources and mobility of metal pollution associated with historical mining in a carboniferous upland catchment, located in the Northern Pennines in the UK. From chemical analysis and geochemical modelling I identified metal sulphates and metal carbonates as the main mineral sources of metals. I also demonstrated that metal carbonates are controlling metal mobility, while seasonality is also producing changes in flow and pH conditions, affecting metal concentrations and behaviour. By using speciation modelling, ecotoxicological assessment tools and *in situ* macroinvertebrate survey I highlighted the dynamics of metals occurring in neutral mine drainage; and suggested the application of environmental quality standards based on bioavailability data within a realistic context relating response of aquatic organisms to river water chemistry and metals. I also evaluated the effects of episodic rainfall on aqueous metal mobility and toxicity to address some knowledge gaps. I found that rainfall conditions did not alter the circumneutral conditions of the catchment, although metal mobility and speciation were affected by the abundance of carbonate and bicarbonate minerals derived from bedrock weathering. I showed that metal toxicity occurred at circumneutral pH, and mainly attributable to zinc. Moreover, I assessed the effects of episodic rainfall in metal toxicity and calculations revealed that short-term fluctuations of metal concentrations are not reflected in the predicted acute toxicity risk to aquatic organisms, underlining the complexity of chemical speciation especially during episodic events. Likewise, I provided a baseline for future mitigation strategies for catchments under risk of metal pollution. Finally, I stressed the importance of the public perception and community involvement in a holistic management of catchments for protecting riverine ecosystems and improving their water quality. Overall, this thesis provides the evidence that a comprehensive metal

assessment requires a great understanding of processes and reactions occurring from metal sources to potential endpoint environments (e.g. water, sediments, and biota). For regulatory purposes, technical knowledge needs to be sensibly transferred to the community for achieving an effective integrated catchment management. Findings from this thesis are suitable for the assessment of streams draining spoil waste areas with similar geochemical conditions and inform future management strategies.

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Abbreviations

AMD	Acid mine drainage
AONB	Area of Natural Beauty
ASPT	Average Score Per Taxon
AVE	Average
AWMN	Acid water monitoring network
AWQC	Ambient water quality criteria
B/D	Below detection limit
BET	Brunauer, Emmett and Teller method
BLM	Biotic Ligand Model
BF	Base flow
BMWP	Biological Monitoring Working Party
CaBa	Catchment based approach
CEH	Centre for Ecology and Hydrology
CI	Confidence interval
DARLEQ	Diatoms for Assessing River and Lake Ecological Quality
DBL	Diffusion boundary layer
DEFRA	Department for Environment Food & Rural Affairs
DGT	Diffusive Gradients in Thin films
DMT	Donnan Membrane Technique
DIC	Dissolved inorganic carbon
DOC	Dissolved organic carbo
DOM	Dissolved organic matter
EC	Electrical conductivity
EDTA	Ethylene diamine tetraacetic acid
EPA	Environmental Protection Agency (US)
EPT	Ephemeroptera, Plecoptera and Trichoptera
Eq	Equation
EQS	Environmental Quality Standard
EQS-B	Environmental Quality Standard based on bioavailability

EQS-H	Environmental Quality Standard based on hardness
ET	Ephemeral tributary
EU	European Union
FA	Fulvic acid
FI	Free ion
FMIF	Free metal ion (function)
F_{TOX}	Toxicity function
$F_{TOX,max}$	Upper threshold of F_{TOX}
$F_{TOX,min}$	Lower threshold of F_{TOX}
HA	Humic acid
HMS	Harmonised Monitoring Scheme
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ISE	Ion-selective electrodes
km	Kilometres
km^2	Squared kilometres
LF	Low flow
LOD	Limit Of Detection
LOIS	Land Ocean Interaction Study
L_T	Lower threshold
Max	Maximum
Min	Minimum
MC	Main channel
M_D	Dissolved metals (e.g. Zn_D)
MPC	Maximum Permissible Concentration
M_T	Total metals (e.g. Zn_T)
M-BAT	Metal bioavailability assessment tool
NRA	National Rivers Authority
NGR	National Grid Reference
NMD	Neutral mine drainage
NICA	Non-Ideal Competitive Adsorption

NOEC	No Observed Effect Concentration
ND	Not detected
NM	Not measured
p	p-value (calculated probability)
pCO_2	Partial Pressure of Carbon Dioxide
PEC	Predicted Effect Concentration
PF	Peak flow
PHREEQC	PH (pH), RE (redox), EQ (equilibrium), C (program written in computer code)
PNEC	Predicted No Effect Concentration
PPF	Post peak flow
PT	Perennial tributary
r	Coefficient correlation
R^2	Coefficient of determination
RBD	River Basin District
RBMP	River Basin Management Plan
RCR	Risk characterisation ratio
RIVPACS	River Invertebrate Prediction and Classification System
SCAMP	Surface Complexation Assemblage Model for Particles
SD	Standard deviation
SEPA	Scottish Environment Protection
SI	Saturation index
SENESCYT	National Secretariat of Higher Education, Science, Technology and Innovation of Ecuador
SPM	Suspended particulate matter
SR	Species richness
SSD	Species sensitivity distribution
TBM	Toxicity Binding Model
TD	Total dissolved
TIMS	Thermal Ionization mass spectrometry
TOC	Total organic carbon
UK	United Kingdom

UK-TAG	UK- Technical Advisory Group
US	United States
UT	Upper threshold
WATEQ4F	Aqueous Speciation-Saturation Model
WFD	Water Framework Directive
WHAM	Windermere Humic Aqueous Model
WHAM-F_{TOX}	Windermere Humic Aqueous Model (toxicity function)
XRF	X-ray Diffraction
XRF	X-ray Fluorescence

Chapter 1: General Introduction

Worldwide, rivers have been the centre of anthropogenic activities. From prehistoric times through to the present day these natural resources have been greatly polluted with significant impacts on its hydrology, ecology and sediment dynamics (Hudson-Edwards et al., 1999a; Horowitz et al., 1993; Macklin, 1996; Nagorski et al., 2002; Miller et al., 2004; Fernandes et al., 2016). Historical metal mining that has produced severe damage to riverine ecosystems and discharged water from ancient mines is considered one of the major causes of point and diffuse pollution in many catchments (Hering et al., 2010).

In the United Kingdom (UK), particularly in the North Pennines, metal mine drainage has been transported as dissolved and associated forms, affecting water and sediment quality (Byrne et al., 2012; Jones et al., 2013; Tame et al., 2017). Ecological and global public health concern has increased as metals can be transferred, bioaccumulated and magnified through to higher trophic levels, producing important risks for human health (Solà et al., 2004). Most efforts have been focused in mitigating effects of abandoned coal mines but little attention has been paid to non-coal mines (metal mines) (Jarvis, 2014). An important number of non-coal mine waters remain untreated in the UK, precluding their compliance with national water quality standards (Han et al., 2013; Potter et al., 2004; Mayes et al., 2008; 2009b; 2010).

A correct understanding of hydro-chemical processes, post-mining metal dispersion and speciation variability is important for river management plans and to formulate site remediation strategies in polluted areas affected by historical mining (Hudson-Edwards et al., 1998). In the last few decades, a variety of analytical techniques and models have been developed to understand concentrations, distributions and chemical behaviour of metals in aquatic environments (Hudson-Edwards et al., 1999b; Paquin et al., 2002; Zhang and Davison, 2015). However, within rivers metal assessment is very complex due to the dynamic of metals in response to certain water chemistry conditions, their

mobilisation through sediments, and the presence of metal mixtures influencing bioavailability and toxicity in aquatic organisms (Gozzard, 2008; Butler, 2009).

This study focuses on Hebden Beck, a river affected by historical lead mining in the United Kingdom. In this area lead production reached its peak around 1861-1862; metals released from ore processing have been dispersed to soils, stream and groundwater due to processes like weathering, erosion and leaching, affecting the surrounding watercourses. Hebden Beck is a sub-catchment (~12 km long) of the River Wharfe located in the northern Pennines region (site description in Chapter 2, section 2.2). Previous studies on metal pollution in Hebden Beck have shown a metal enrichment of dissolved Zn (2003 μg/L), Ba (971 μg/L), Pb (183 μg/L) and Cd (12 μg/L) reducing water quality (Jones et al., 2013).

The size and accessibility of Hebden Beck catchment, the presence of point and diffuse sources of metals, and the limited influence of other sources of pollution, provided a good scenario for a comprehensive catchment-scale assessment of metal speciation, transportation, bioavailability and potential ecotoxicity. Thus, the overall aim of this research was to assess metal contamination derived from historical mining by evaluating sources, mobility and toxicity in river water to support strategies for improving water quality and ecological conditions.

This chapter provides an overview of metal contamination from historical mining in the UK, particularly in the North Pennines. Section one describes historical mining in the UK, geological characteristics of the Pennines, mining techniques and their socioeconomic legacy in Wharfedale. Section two compiles information about metal contamination of rivers and environmental legacy of historical mining in Wharfedale. Section three includes a brief description of the environmental services of the Wharfe catchment. Section four gives an overview of UK Environmental Directives, including the Water Framework Directive. Section five describes the most relevant water quality monitoring programmes in the UK. Section six refers to the traditional and current methods applied in the study of metal sources, behaviour and bioavailability. Section seven provides a brief introduction to remediation techniques in freshwater (particularly in neutral mine

drainage). Section eight details the site selection process and the map/tables of site locations. Section nine introduces the aim and specific objectives of the thesis and section ten provides the thesis outline.

1.1. Historical Mining in the United Kingdom

Mining has been carried out in the UK since the early Romano-British period (1st century AD) and represented a key feature in the Industrial Revolution of this nation in the eighteen century. Historically, mineral deposits have been mined in Cornwall, Devon, the Mendips Hills, North and Central Wales, Shropshire, the Northern and Southern Pennine Orefields, the Lake District and the Southern Uplands of Scotland (Scott, 2001). The main minerals exploited in the country were Pb, Zn, gold (Au), silver (Ag), iron (Fe), manganese (Mn), copper (Cu), tin (Sn), tungsten (W), arsenic (As) and antimony (Sb). The transition of manufacturing processes at this time transformed lead (Pb) mining from a small subsidiary enterprise into a major industry as it was used for public constructions including farmhouses and cottages, reservoirs for water storage and piping. In the eighteenth and nineteenth centuries the lead industry was fully established allowing the development of large companies and mining communities. However, the industry gradually declined as result of the development of large mines in Spain and United States of America (Gill and Burt, 2003).

The methods used for mining in the UK evolved progressively. Early activities were opencast with ore extraction being performed on the soil surface where galena (lead sulphite) veins were uncovered by physical events such as rainfall (Raistrick and Jennings, 1965). As superficial deposits were exhausted, underground methods were adopted for mineral removal from vertical veins. Accordingly, during the early years of mining it was common to crack the rock by heating and cooling processes using flaming torches and water or vinegar, respectively. The auxiliary tools for this method of ore extraction included the pick, the hammer and the wedge. During the seventeenth century, the introduction of gunpowder enabled the construction of deeper adits and levels to remove the ores, to drain the mines and to sink shafts. Those shafts provided access, ventilation and ore removal pathways through interconnected underground tunnels. Earlier shafts were dug on the mineral vein, but later were sunk in barren wall rock. This later system was known as Bell Pits, and allowed the minerals extraction from the vein without affecting the shaft's stability (Waltham, 2007). The haulage of minerals within the mine and to the surface was

done initially using horses; later the activity was performed successively with hydraulic power and steam powered machines.

With regard to hydraulic methods, a technique called “hushing” was used to scour away the soil by erosion and separate lead minerals from lighter rock. Waterwheels were used as multi-purposes machines for pumping water and crushing and winding the ores. The use of water in mining required the construction of reservoirs to store water that was released through artificial channels known as “leats” (Fairbairn, 2002). Once lead ores were extracted they were transported to the dressing floors. In this area the ores were sorted, crushed, separated and bagged for the smelt mill (Raistrick and Jennings, 1965). In the mill, minerals were melted to remove impurities. The smelting process could be accomplished through two techniques: the ore-hearth or the reverberatory furnace. The selection of these techniques was based on the amount of ore, fuel availability and type of impurities in the mineral. The ore-hearth was a flue where the ore and fuel (peat) were mixed; for its efficient operation a blast of air was supplied by waterwheels. The reverberatory furnace was generally much larger, where fuel (coal) and ores were kept separately, and the heat was transmitted by gasses for melting the minerals (Burt, 1984). Beside the economic benefits of mining, one of the major problems from this activity was the metal pollution of the areas where the activity was developed (Potter et al., 2004).

1.1.1. Historical metal mining in the Pennines: Wharfedale

The Pennines comprise a range of hills with a total length of approximately 250 miles (400 km) that divide North West and North East England. Their landscape consists of upland and lowland areas, and several rivers that drain the main watersheds in northern England. The fluvial complex includes the Rivers Eden, Ribble, Irwell and Mersey that flow westwards towards the Irish Sea, and the rivers Tyne, Tees, Wear, Ure, Nidd, Calder, Wharfe, Aire, Don and Trent that flow eastwards to the North Sea. The Pennines are part of three National Parks (The Peak District, The Yorkshire Dales and Northumberland) and Areas of Outstanding Natural Beauty-AONB (the North Pennines, Nidderdale), therefore

this region is widely considered to be one of the most scenic areas of the United Kingdom (North Pennines AONB Partnership, 2013).

The North Pennines were designated as AONB in 1988 and UNESCO Global Geopark in 2004, due to their particular moorland scenery which is the product of centuries of farming and lead-mining (Dunham, 1988; Zouros and McKeever, 2004). The North Pennines are bordered by the Tyne valley to the north, by the Yorkshire Dales to the south, by the Durham lowlands to the east and by the Eden Valley to the west (Lawson et al., 2011). The special character of the North Pennines landscape has its foundation in the underlying rocks and the geological processes which have shaped it over hundreds of millions of years of Earth history. Tropical seas, deltas, rainforests, molten rock, deserts and ice sheets have all played a part in creating the bare bones of the landscape. The deep roots of the North Pennines are slates and volcanic rocks (Weardale Granite- 400 million years ago) and together with abundant mineral veins and deposits are known as the Northern Pennine Orefield (North Pennines AONB Partnership, 2013).

In the Carboniferous period (350-300 million years ago) the lime sediments (skeletal fragments of marine organisms) became limestone, the mud and sand became shale and sandstone, and the forests turned to coal. Periodically, the sea flooded in, drowning the deltas and depositing limestone again. This cycle happened many times, building up repeating layers of limestone, shale, sandstone and thin coal seams, known as ‘cyclothems’. About 295 million years ago the Whin Sill was formed by molten rock, injected between layers of sandstone, limestone and shale. The molten rock cooled and solidified producing vertical cracks seen in cliffs and quarry faces (Figure 1.1). The veins of minerals formed about 290 million years ago when mineral-rich waters, warmed by heat from the buried Weardale Granite, flowed through underground fractures. Once the fluids cooled, dissolved minerals crystallized within the fractures, forming mineral veins. Sometimes the fluids reacted with limestone on the sides of the fractures, altering the rock and forming mineral deposits known as ‘flats’ (North Pennines AONB Partnership, 2013). The foundation of the area’s economy during the eighteenth and nineteenth centuries derived from the abundance of

mineral deposits. Galena (lead-sulphide ore) mining was the most important activity in this area, although commercially mined minerals also included, sphalerite (zinc-sulphide ore), iron ore, fluorite/fluorspar (calcium fluoride) and barium as barite (barium sulphate) and witherite (barium carbonate).

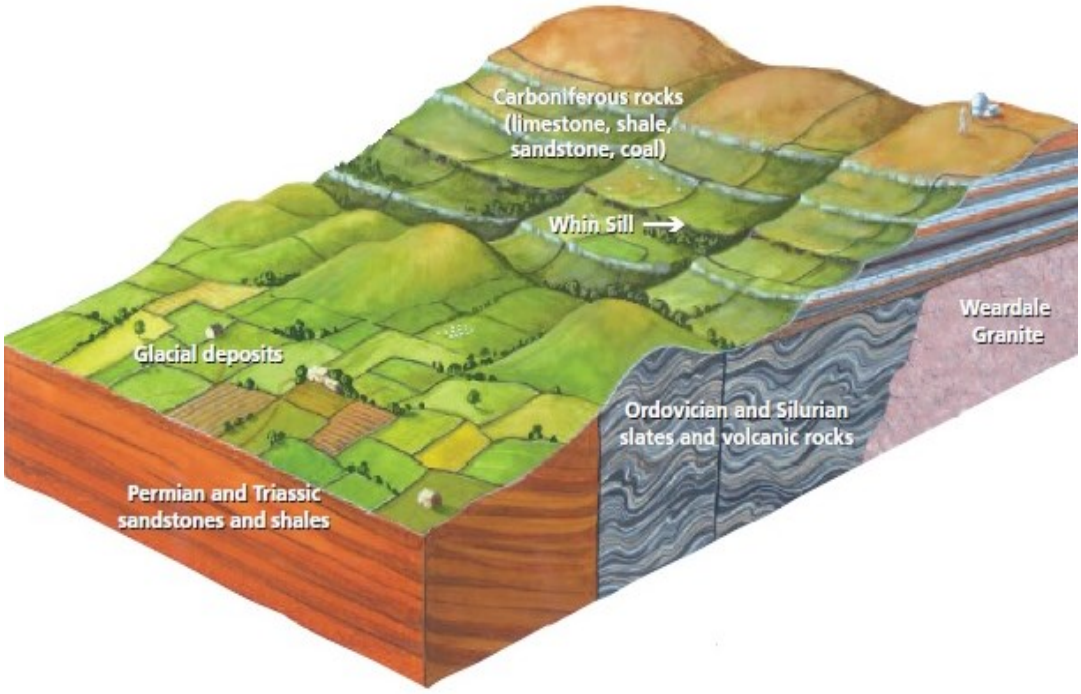

Figure 1. 1. Schematic diagram of the North Pennine escarpment showing the underlying geology and its influence on the landscape. From Elizabeth Pickett © NERC.

In the North Pennines, intensive lead mining was developed in the Swaledale and the Wharfedale valleys. In Swaledale one of the main mining activities was concentrated near Gunnerside Beck and Barney Beck tributaries of the River Swale (Dunham and Wilson, 1985), whilst in Wharfedale one of the main ore extractions was performed around Hebden Beck, a tributary of the River Wharfe (Figure 1.2). Hebden Beck rises from Grassington Moor and drains an area of 26 km^2 until its confluence with the River Wharfe. Several towns and villages are located in Whaferdale including Wetherby, Ilkley and Otley as the most populated, between others with lower population like Grassington, Hebden, and Conistone. The River Wharfe flows into the Ouse which further downstream joins the Trent to form the Humber Estuary, and is the largest catchment of the English east coast which discharges into the North Sea.

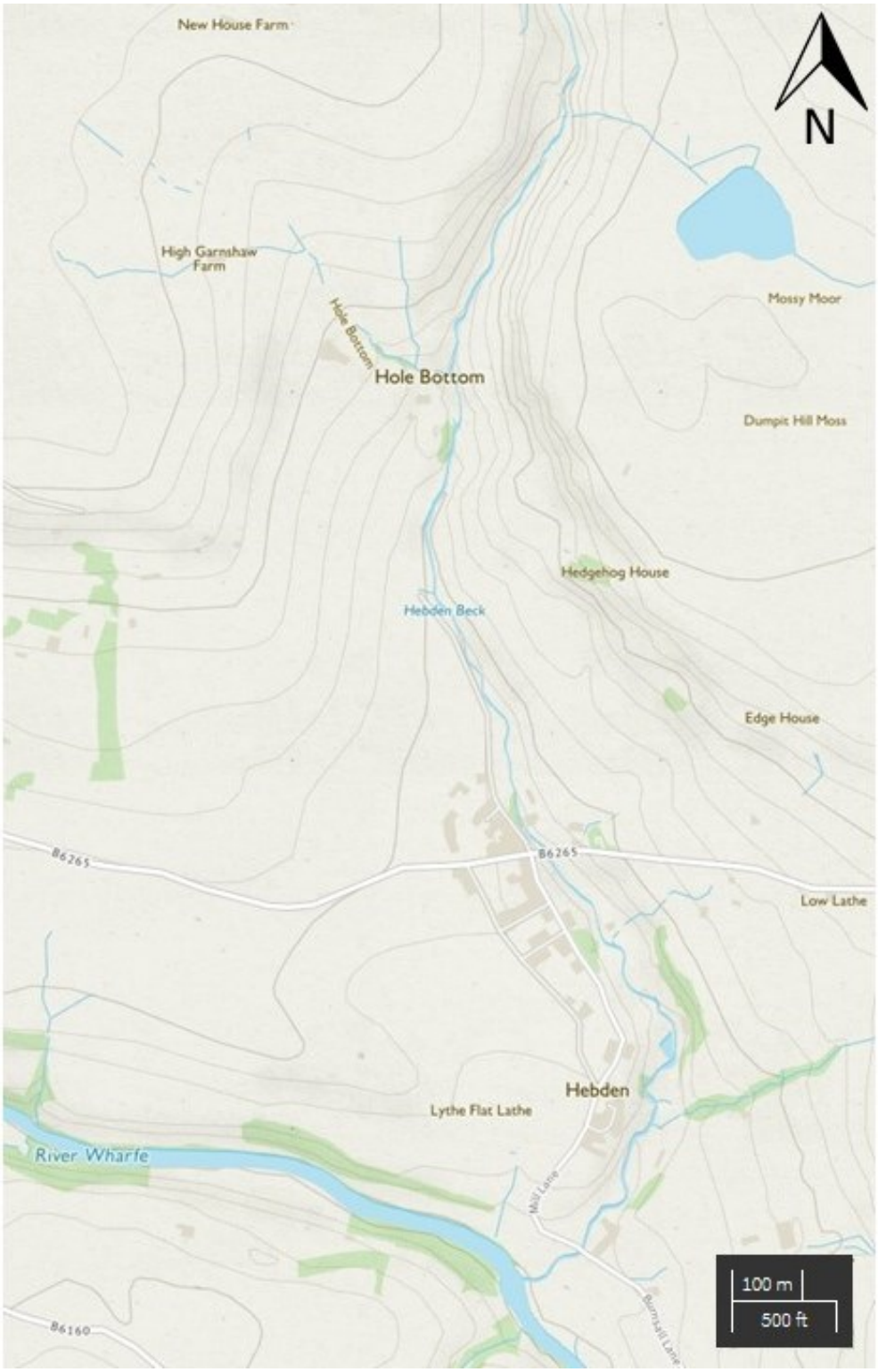

Figure 1. 2. The River Wharfe showing Hebden Beck as tributary. Ordnance Survey Map (Grid Ref: SE 0295563316). Contains OS data © Crown copyright and database rights 2017.

The earliest mining in Wharferdale and around Grassington comprised two areas named Yarnbury and New Rake, and later many other areas were also highly exploited (Figure 1.3). In Hebden, levels were designed to give natural drainage for Grassington mines (e.g. Lanshaw, Duke, and Charter). Table 1.1 shows a list of mines located in this area which are usually referred to collectively as Grassington mines (Gill, 1993).

During the medieval period, as in other rural communities of the UK, mining on the Wharfedale was performed at relatively small scale. Local families leased small blocks of ground along mineral veins known as Meers which were under the Customary Mining Law and were owned by the British Crown (Gill, 1994). Within the Wharfedale region, some mining villages were considered as the King's field; other villages like Kettlewell, Conistone and Hebden were under local holders (Barmaster) supervision. In the sixteenth century, lead extraction increased in the area, so the development of efficient mining methods was required. In 1640, mining experts from Derbyshire, Swaledale and Cornwall moved into the villages of Grassington and Hebden. Important innovations were introduced, for example extensive integrated water management system and the use of wire as ropeway power for pumping and winding (Gill, 1993).

Table 1. 1. Mines in Grassington (Gill, 1993).

Area	**Mines**
Old Pasture	Blackhil, Blew Level, Cockbur, Ellerbeck, Loss Gill Bank, New Rake, North Rake, Yarnbury
New Pasture	Frankland Fold, Pikehaw, Hecklar Rake, Grime Grooves, Chelsea,Cricket, Fiddler Plet, Folly, Green Plet, Greenwich, Plet Head,Stool, Three Footed Stool, Sword and Pistol, Smiling Fancy,Pawfrey, Green Bycliffe
Out Moor	Brown Bycliffe, Burnt Ling, Bycliffe, Castaway, Coalgrovebeck,Coalgrovehead, Fourteen Meers, Glory, Gregory, Legerins, NewRipon, Pipper Plet, Pit Moss, Ridley Old Work, Ripley Vein,Rippon, Rushbob, Six Meers, Three Meers, Turf Pits, Wash Vein, Wilkinson Pits

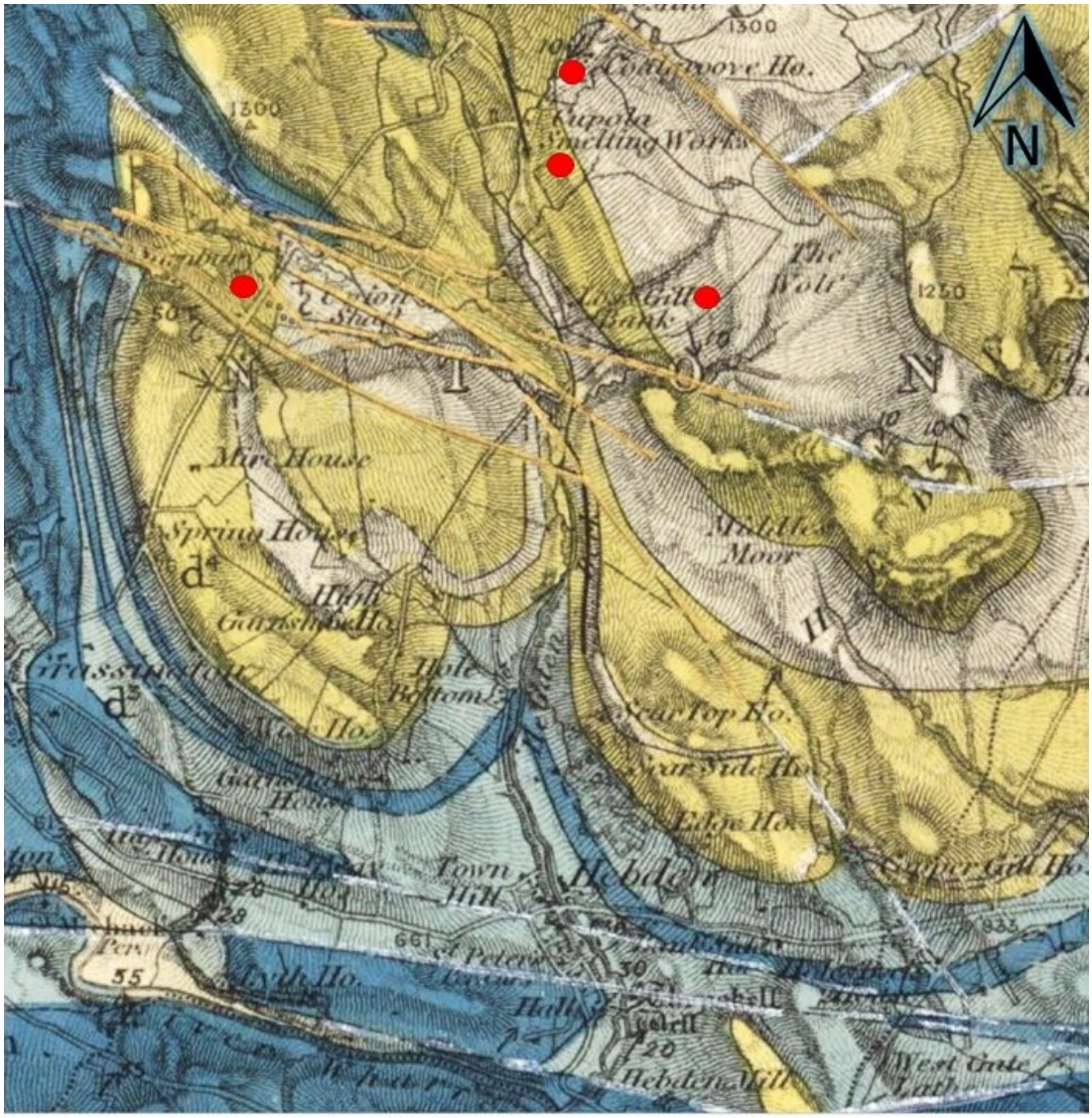

Figure 1. 3. Geology and mineral veins from Grassington and Hebden area. Mineral veins are shown as gold lines, faults as white lines and uncertain faults and boundaries as broken lines. Red dots show some mining structures (e.g. Yarnbury mine and Cupola smelting mills). Geological Survey of England and Wales 1:63,360 geological map series [Old Series]. Reproduced with the permission of the British Geological Survey ©NERC. All rights Reserved.

From 1758 the Grassington mines were restructured under the administration of the Duke of Devonshire. Better ventilation and more efficient ore and waste transportation were achieved through the excavation of a long adit (2.5 km) known as The Duke's Level. A number of reservoirs called The Blea Beck Dams were built to minimize water supply problems during dry weather. An extraordinary smelting mill was also built in 1792 to serve the lead mines. This structure, called The Cupola Mill, had a flue length of around 1.7 km, including a network of flue systems, condenser chambers and a chimney. In addition, it had two reverberatory furnaces (cupolas) that isolated the processed mineral from contact with fuel. The cupola smelt mill supported the lead ore processing by using coal instead of the traditional peat or wood (Gill, 1993; Raistrick and Jennings, 1965).

During the eighteen century, Yorkshire lead mines played an important role in the UK lead production. Between 1845 and 1865 this region provided an average of 10 per cent of the national production (Table 1.2) with Grassington mines producing around 20,000 tons (~20,300 metric tonnes) (Gill and Burt, 2003). After this period, lead production declined dramatically, as it became more difficult and expensive to extract. At the same time, new, shallow and metal rich mines from the United States of America, South America, Africa, Australia, the Middle East and Europe (Spain), provided higher amounts of ore with cheaper costs. As a result, Yorkshire mines stopped underground activity around 1870 and only the smelt mills continued working (Flynn, 1999).

Table 1. 2. Data regarding Yorkshire and U.K. lead metal production from 1845 to 1913 (Gill and Burt, 2003).

Year	Yorkshire Metal (tons)	U.K. Metal (tons)	% of U.K. Lead production
1845-1854	5,213	59,040	10
1855-1864	6,905	67,380	10
1865-1874	4,976	66,340	7
1875-1884	3,341	52,230	6
1885-1894	1,518	34,300	4
1895-1904	490	23,730	2
1905-1913	92	20,866	0.4

The principal smelt companies functioning in this area were the Grassington Lead Mines Ltd, the Hebden Moor Mining Co., and the Dales Chemicals Ltd. The London Company, famous as the largest and best equipped in the UK, also had affiliates in the area. Since 1880, mines have been closed with no attempt to reopen again. However, between 1916-1920 and 1956-1963 the Grassington Lead Mines Ltd and the Dales Chemical Company carried out some spoil reprocessing campaigns where barytes and fluorspar were primarily recovered (Gill, 1993; 1994).

Nowadays some of the ancient buildings associated with mining activities in Wharfedale have become structures of archaeological and cultural importance for the region. Many abandoned mines represent important heritage sites which have been classified as Scheduled Ancient Monuments (White, 1998). Specifically around Grassington and Hebden, a large number of mining structures have been identified which have become the central attention for tourists (Yorkshire Dales National Park, 2006; North Pennines AONB Partnership, 2013).

1.1.2. Socioeconomic influence of mining in rural communities: Wharfedale

In the eighteenth century the Industrial Revolution in the United Kingdom produced a drastic transformation in living conditions. Changes from a rural economy based on agriculture and farming to industrialized practices produced a massive effect on the economy and social facets in the population (Landes,

1969). In the North Pennines mining industry had a multiplier effect in rural communities (Hallas, 1999). In fact, mining changed the work patterns by transforming farming communities into communities of miners. Labour priorities changed as farmers spent less time on fields and more in mining jobs (Table 1.3). In the mining industry miners were divided in three main roles: i) deadmen who drove levels and sank shafts, ii) pickmen who extracted the ores and iii) dressers who washed the minerals. Other occupations were level-wallers, machinemen and those involved in moving material out of the levels. The smelters, refiners and craftsmen made up the rest of the mining workforce (Hunt, 1970).

Table 1.3. Male mine workers in Grassington and Hebden from 1841 to 1871 (Hallas, 1999).

Villages	Year	No. of Lead miners	Total male population	% of lead miners
Grassington	1841	146	544	27
	1851	103	563	18
	1861	128	492	25
	1871	63	401	16
Hebden	1841	27	248	11
	1851	46	236	19
	1861	85	225	38
	1871	56	195	29

Economic inequality was also an important effect of mining (Hunt, 1970). Despite the miner's expertise their economical remuneration was not based on their working hours and health risks. The agreed wages resulted from a deal depending on the mine difficulty and the distance from veins to shafts. Moreover, miners frequently paid for their own working materials such as candles and gunpowder, and services such as transporting and dressing the ore (Raistrick and Jennings, 1965). Statistical evidence of lead-miner's wages is scarce, fragmented and difficult to interpret due to the varied payment system from each company. Generally, wages were provided in monthly, quarterly or half-yearly intervals. This system kept mineworkers constantly in debts as they need anticipated payments for their daily living costs (Sigworth, 1992).

Cotton and linen textiles manufacturing was another form of industry in the area providing an income independent from lead mining wages. Until 1871 those

activities existed together with small scale agriculture, and house holders recruited a significant workforce (Table 1.4). This business diversification helped rural communities to face the losses caused by closing of mining industry (Hallas, 1999). For instance, in Grassington current industries are related to accommodation, food services, leisure and human health (Office for National Statistics-UK).

Table 1. 4. Percentages of the working population in three main occupations in Grassington (1851-1891) (Sigworth, 1992; Gill, 1993).

Occupation	**Census Year**				
	1851	**1861**	**1871**	**1881**	**1891**
Lead mining	23%	31%	21%	10%	3%
Textiles	29%	12%	16%	6%	5%
Agriculture	14%	17%	23%	32%	36%
Other	34%	40%	40%	52%	56%

The health of miners was drastically affected by mining activities (Oliver, 1893). Respiratory diseases were accentuated when gunpowder was discovered. Boys and women developed severe disorders as result of overtiredness and heavy works. Medical reports from Grassington have mentioned retarded puberty, digestive problems, and distortions in legs, spinal column and pelvis (Raistrick and Jennings, 1965). These conditions reduced worker's lifetime compared with other contemporaries from different occupations. Overcrowding in local farms or cottages provided to miners to live near to mining fields was another factor impairing the health condition of miners (Raistrick, 1953).

From the eighteenth century some mining companies became concerned about their worker's well-being and provided notable support to social and health services (Raistrick, 1973). For example, the London Lead Company helped in the foundation of the Greenhow Hill village for the accommodation of miner's families. It also created a wide number of policies to improve the quality of life from the miners and their families. Through these policies a monthly minimum wage was guaranteed, food supplies were subsidized, likewise free medical care and social security funds were provided. Furthermore, in 1842 the Parliament of the United Kingdom also introduced important working reforms, for example they created the Mines Act which prohibits any girl or woman to work underground in metal

mines, boys were allowed to work on dressing floors according with the company policies (Raistrick and Jennings, 1965).

The closing of mining activities was an important factor for population emigration. Even though lead mining was not the only industry in Grassington and Hebden, between 1851 and 1881 the population of Grassington's village declined about 400 people (Gill, 1994; Sigworth, 1992).

1.2. Metal contamination of rivers and Environmental Legacy of historical mining in Wharfedale

1.2.1. Metal contamination of rivers

River systems surrounded by mining areas can become contaminated through diverse metal behaviours. One source of river contamination by metals is *in situ* chemical weathering of contaminated soils, alluvium and mining wastes caused, by flooding and fluctuation of water levels in floodplains. These processes may be accelerated by changes in the pH and redox potential (oxidation or reduction) (Luoma and Rainbow, 2008). In mine drainage waters the concentration of metals and pH depends on the oxygen supply, grain size, composition of metal sulphides, iron-sulphur oxidising bacteria, temperature and acid solutions neutralisation (Rose and Cravotta III, 1998). Acid mine drainage (acidic pH) can cause dissolution of metals carrying silicate, carbonate, sulphide and oxide minerals by releasing their metals to the solute phase. Oxidising conditions cause breakdown of metal-carrying sulphide minerals (Hudson-Edwards, 2003). Conversely, reducing conditions in river sediments can encourage the formation of insoluble metal sulphides (Cd, Cu, Pb, and Zn) decreasing their bioavailability and toxicity to aquatic life (Hudson-Edwards et al., 1998). Mine drainage flowing through limestone host bedrock produces neutral mine drainage where major ion concentrations reflect the mineralogy of the bedrock, generating metal-rich effluents but with circumneutral pH (Byrne et al., 2012; Jones et al., 2013). Hence, the importance of studying the geologic setting, local water chemistry, kinetic rates and permeability of ore and gangue minerals (Navarro et al., 2015; Plumlee et al., 1999).

Sediments are extremely important in the transport and cycling of metals within the fluvial system (Salomons and Förstner, 2012; Horowitz, 1991). Metal concentrations in sediments are usually considerably higher than those observed in the dissolved phase because metals are likely accumulated by fine-grained material. Therefore, riverine metal fluxes can be dominated by fluvially transported sediments (Horowitz, 1991; Macklin and Klimek, 1992). Between 30 and 98 % of the total metal load of a river can be transported in a sediment-associated form (Gibbs, 1973; Salomons and Förstner, 2012). Sediment-associated metals are not static within the fluvial environment. Instead, they are influenced by a range of physical and chemical processes that control their behaviour, mobility and concentrations in the environment.

Another input of river contamination by metals is high flow events at abandoned mines where spoil wastes and tailings are commonly deposited next to rivers. These highly contaminated materials can be mobilised during rainfall and erosion by high river flows through the discharge of particulate metals into the water column. In addition, when floodplain alluvium is eroded, superficial contaminated sediments are in contact with water causing metal desorption from sediment to the aqueous phase. Nagorski et al. (2002); Macklin (1996); Miller (1997) have documented that metal dispersal and storage is controlled by physical and chemical factors such as hydrological and attenuation processes (Chapter 4). Additionally, some studies have outlined that mining waste drives significant impacts on fluvial geomorphology such as gradient and channel width, controlling the ability of the river to transport sediments (Hudson-Edwards et al., 1999c; 2001; Miller et al., 2004; Low et al., 2005).

1.2.2. Environmental legacy of historical mining in Wharfedale

The ancient mining activities in the United Kingdom are the main drivers for metal pollution in water and flood plain soil (Johnston et al., 2008). Abandoned mines, particularly, represent a major diffuse source of metal pollutants (aqueous or particulate forms) as metals spread through groundwater and surface water across dozens of kilometres (Macklin, 1997; Macklin et al., 1997; Miller, 1997; Hudson-Edwards et al., 1999b; Mayes et al., 2015). According to a report from

the Environment Agency (2005) England and Wales have the most affected rivers for metal contamination. Those rivers included the Tyne, Wear (Northumbria River Basin District or RBD), Swale, Ouse (Humber RBD), Rheidol, Ystwyth, Conwy, Afon Goch Dulas (Western Wales RBD), Clywedog (Dee RBD), Wye, Yeo, Axe (Severn RBD), Fal, Fowey, Tamar (South West RBD), Newlands Beck (North West RBD) and Glenridding Beck (Solway-Tweed RBD).

Metal contamination of river sediments has been extensively studied in the United Kingdom (Byrne et al., 2010; Shepherd et al., 2009; Hudson-Edwards et al., 1998; Owens et al., 1999; Hudson-Edwards et al., 1999b; Miller et al., 2004; Low et al., 2005; Tame et al., 2017). High concentrations of bismuth (Bi), cobalt (Co), gallium (Ga), lithium (Li), molybdenum (Mo), niobium (Nb), antimony (Sb), tin (Sn), vanadium (V), Yttrium (Y), zinc (Zn) and zirconium (Zr) have been reported in the uppermost zones of the River Swale. Similarly, high concentrations of Ag, Ba, cadmium (Cd), manganese (Mn), nickel (Ni), Pb, strontium (Sr) and Zn have been also found in the downstream tributaries of this river (Dennis, 2005). Likewise, elevated concentrations of calcium (Ca) and copper (Cu) were observed in the area of Richmond a town located on the River Swale while high levels of Ca and magnesium (Mg) were also found in the Vale of York located in Yorkshire (Stanley, 1998).

It is known that the pollution of rivers by metals include a variety of negative impacts on sedimentological and hydrological processes that in turn could influence the ecology and biology of certain species (Byrne et al., 2012). The River Swale is an example of these impacts. In this area, native plants species have been reduced in population number and animals such as sheep have suffered health impairment due to the ingestion of toxic metals accumulated in plants (Allcroft, 1956; Brewer et al., 2005). Despite this finding, studies concerning metal uptake in this zone are still scarce (Dennis, 2005).

In relation to mining pollution in the river Wharfe, Neal et al. (1997) reported concentrations of dissolved Pb (1.51 μg/l) and Zn (16.7 μg/l). In one of the tributaries of Hebden Beck, elevated metal concentrations of dissolved Zn (2,003 μg/L), Ba (971 μg/L), Pb (183 μg/L) and Cd (12 μg/L) have been reported in the

area in recent years (Jones et al., 2013). As a consequence, the status of surface water in Hebden Beck has been reported as moderate regarding ecological and biological criteria based on the assessment of chemical and physicochemical parameters, and the status of macroinvertebrates and algae communities; while for ground water the overall chemical status was poor (Barber, 2014). Thus, strategies for the systematic identification and prioritisation of polluting sites for remediation based on robust scientific evidence are essential for the effective, defensible deployment of public funds.

1.3. Environmental services of the Wharfe catchment

The Wharfe catchment is generally rural with small, scattered settlements. The Upper Wharfedale is similar to other areas at the Pennine uplands and the Yorkshire Dales National Park where agriculture is primarily sheep grazing. It is extensively used for public water supply and irrigation, both from reservoirs and by river abstraction. At the same time, this catchment offers a number of recreation opportunities including water-based activities like coarse fishing, canoeing and boating. In addition, bankside recreation is also common such as bird watching, riverside walking, cycling and trekking (North Pennines AONB Partnership, 2013).

The Wharfe catchment has 50 natural water bodies and 24 that are artificial or heavily modified. In 2009, 17% of its rivers achieved good or better ecological status/potential. For biological status, 24% of rivers reached good/better status, 24% presented poor status and 9% bad. Water quality failures are mainly attributed to diffuse pollution (e.g. agriculture, mining) and point source discharges (e.g. water industry sewage works). Physical modification of water bodies for storage, supply and flood protection also play an important role in the status of this catchment (North Pennines AONB Partnership, 2013; UK-Environment Agency, 2015).

1.4. Overview of UK environmental directives

Legislation governing the mining industry has grown over the years. This has often followed a major event or disaster which has led to calls for specific legislation to control or eliminate certain operations within the industry (Hering et

al., 2010). In Britain, legislation is ratified by Acts of Parliament; these are further refined by Regulations, which explain, extend or amend the parameters to which the relevant Act will apply. Early environmental protection legislation in the United Kingdom included the Rivers Pollution Prevention Acts of 1876 and 1893, which were introduced to control the discharge of metals from mining activities into the fluvial environment (Haworth, 1906).

As the mining industry flourished in different places of the country, additional legislation was created to ensure planning for abandoned mines (e.g. The Coal Mines Regulation Act and Metalliferous Mines Regulation Act in 1872). Regulations to deal with a variety of environmental issues related to abandoned mines, water and atmospheric pollution were promoted by the Control of Pollution Act (COPA) in 1974. Later, the Water Law was consolidated in 1989 and updated to create the Water Industry Act in 1991, Water Industry Act in 1999, and the Water Act in 2003 (Hallett et al., 1991). The Environment Agency was created in 1996 according with the Environment Act from 1995 for protecting and improving the condition of the environment in England.

Between 1990 and 2010, several improvements were promoted within the European environmental legislation. The creation of Regulatory Bodies and Directives e.g. the integration of many European directives, including: the Water Framework Directive (2000/60/EC), Marine Directive (2008/56/EC), Groundwater Directive (2006/118/EC), Nitrate Directive (91/676/EEC), and Pesticide Directive (2009/128/EC) helped to ensure the responsible use of natural resources and contribute to the basis for UK regulations (Hering et al., 2010).

1.4.1. UK Water Framework Directive

The European Water Framework Directive (WFD) came into force in December 2000 and became part of UK law in December 2003 (European Commission, 2003a). This legislation promotes the achievement of a good ecological and chemical status in all inland, estuarine and coastal waters by 2015. It also provides the basis to improve the water environment through the implementation of River Basin Management Plans (RBMPs) within the administration of the River Basin Districts (RBD) (UK-Environment Agency, 2015).

In this context, water quality status is described in the RBMPs (UK-Environment Agency, 2015). For the RBMPs, the characteristics of water bodies are measured by using biological, chemical and physical standards (UK-TAG, 2009). For surface water status two criteria are considered, the ecological and the chemical status. The ecological status is assessed according to: i) biological quality (e.g. fish, benthic invertebrates, and aquatic flora), ii) general chemical and physico-chemicals quality (e.g. specific pollutants, temperature, oxygenation, nutrients) and iii) hydromorphological quality (e.g. river bank structure). The chemical status is defined by Environmental Quality Standards (EQS) which are based on laboratory toxicity tests from a “priority list of substances”, providing scientific criteria for chemical regulations (e.g. heavy metals) (Figure 1.4).

For groundwater bodies, the classification approach is different from surface water bodies. Each groundwater body requires the classification for its chemical and its quantitative status. Both have to be classed as either 'good' or 'poor'. Chemical status indicates the effects of pollutants in groundwater while quantitative status indicates the impacts from human activities like changes in the groundwater flows for water abstraction to other water bodies (UK-TAG, 2008). In addition, the ecological quality in rivers is assessed by the River Invertebrate Prediction and Classification System (RIVPACS) using data from invertebrate samples. RIVPACS predicts the river invertebrate community that would be found at a site by reference to a database of river sites considered to be the best available of their type.

Assessing the ecological quality as part of water management has inherent difficulties. This is because the value of ecological quality (assumed as the ways in which the natural environment supports human well-being), is often not fully understood or measured to the extent that supports environmental regulations (e.g. WFD implementation) (Vlachopoulou et al., 2014). Thus, better demonstration and communication of the benefits of water-related regulations and the impact of good ecological quality on people's lives is greatly needed (European Commission, 2003b). This becomes a very challenging task that will require appropriate strategies, often time-consuming but essential for an integrated assessment, monitoring and remediation of water bodies (particularly

catchments polluted by point and diffuse sources of metal pollution) for the genuine achievement of WFD goals.

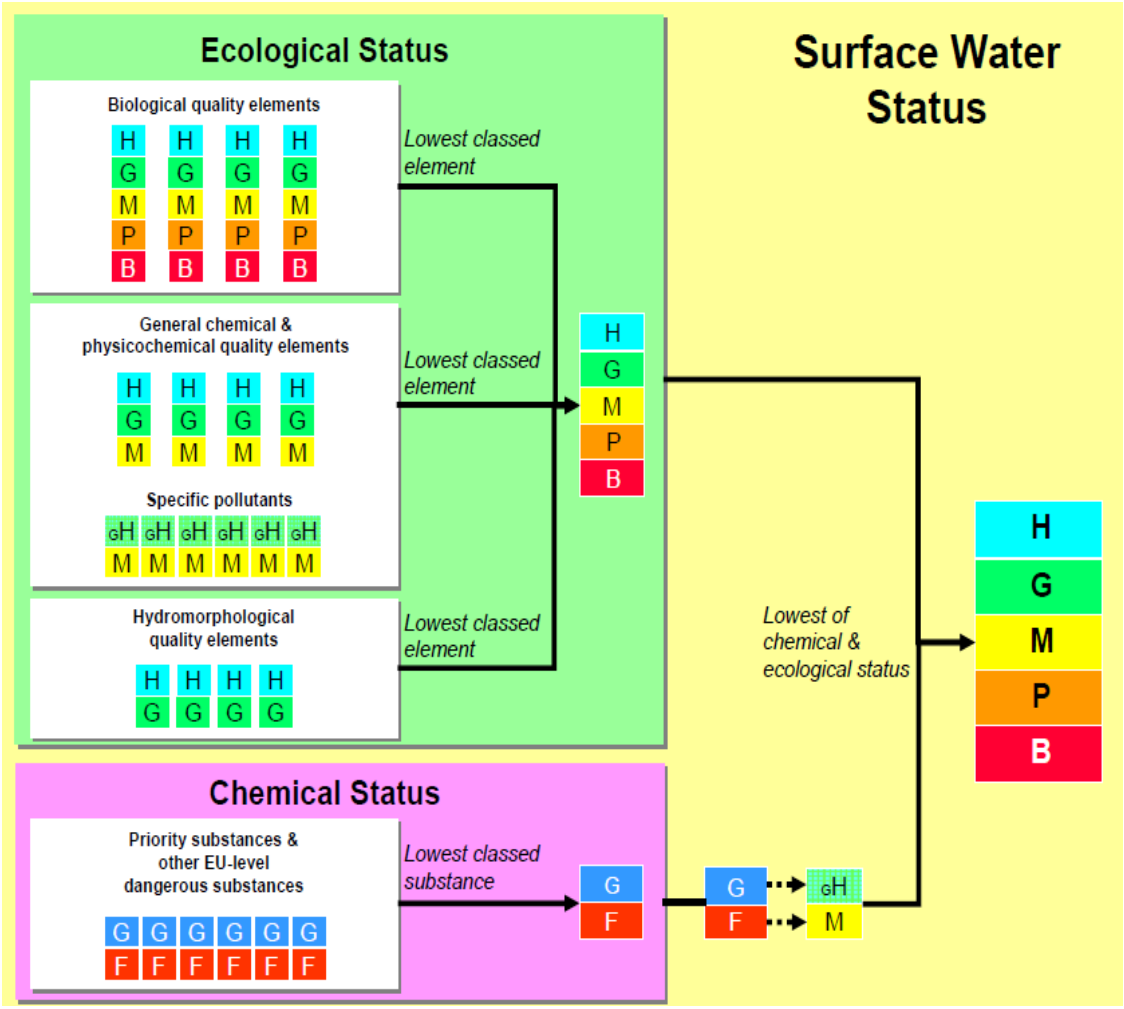

Figure 1. 4. Schematic representation of how results for different quality elements are combined to classify ecological status, chemical status and surface water status as required by the WFD. Key: "H" means high; "G" means good; "GH" means good or better; "M" means moderate; "P" means poor; "B" means bad; and "F" means failing to achieve good surface water chemical status. Surface water status is determined by the poorer of ecological and chemical status; thus if ecological status is good but chemical status is failing to achieve good, then overall surface water status class is "moderate" (UK-TAG, 2009).

1.5. Water quality monitoring programmes

In the United Kingdom the national responsibility for the control of pollution in all inland and coastal waters is divided into three regions: England and Wales, Scotland and Northern Ireland. For the case of England and Wales, the National Rivers Authority (NRA) formed in 1989 was responsible for maintaining and improving water quality and for pollution control, water resources, flood defence and fisheries, navigation, conservation and recreation. In July 1992, the UK Government announced the formation of a single Environment Agency by amalgamating the duties of the NRA with the regulation of solid waste and the on-site control of polluting industrial processes (Davies and Gee, 1993). The Environment Agency is sponsored the Department of Environment, Food and Rural Affairs (DEFRA), that amongst other activities supports a national database of chemical and biological water quality monitoring from around 7,000 sites across England and Wales (UK-Environment Agency and Water UK, 2013).

The monitoring of water bodies in the United Kingdom, particularly within England and Wales has a long history and has typically been divided into three aspects of management: quality, quantity and physical structure. One of the long term monitoring programmes is the Harmonised Monitoring Scheme (HMS), established in 1974 to provide an archive of water quality data, including long-term trends of some determinands (e.g. nutrients and heavy metal) entering the river environment. The HMS is administered by the Environment Agency in England and Wales, and in Scotland by the Scottish Environment Protection Agency (SEPA). It includes 230 sites located at tidal limits of major rivers or at the confluence points of important tributaries.

In 1980, studies about the impact of acid waters on the biology of rivers promoted the establishment of the Acid Water Monitoring Network (AWMN). Since 1988, a database of chemical, physical and biological parameters had being developed at twenty two sites in the UK. This network provides a long-term, high-quality chemical and biological record to assess surface water acidity and their aquatic associated effects (Patrick et al., 1996). In addition, the Land Ocean Interaction Study (LOIS) was designated for water quality monitoring and provided the

opportunity to consider the relationships between land use and water quality (Leeks and Jarvie, 1998; Neal and Davies, 2003). Considering that water quality encompasses many different parameters, including nutrient levels, acid-base chemistry, organic pollutants, pathogens, pesticides, industrial and pharmaceutical products, suspended sediments, colour and temperature, it is difficult to generalise about either the overall direction of change in water quality, or the role of ecosystems in regulating it. Thus, historic data about river quality can be used to demonstrate significant changes within these ecosystems (Brown et al., 1982; Hurley et al., 1996; Beven et al., 2008).

Monitoring programs have identified approximately 3,525 sites as abandoned metal mines with relevant information about their working history and ore mineralogy. These valuable bodies of data have been used to inform the management of abandoned mines which are considered as the most significant pollution threats in the UK. Despite these efforts there are still substantial gaps in some regions. Thus, the Coal Authority was established in 1994 to manage the effects of past coal mining and non-coal mining, like water pollution and other mining legacy issues. In addition, they are also responsible for managing remediation trials such as passive systems (e.g. Force Crag in the Lake District National Park) where metals are removed without the need for added energy or chemicals. Mine water passes through a compost mixture where microbial activity binds the metals as sulphides, before discharging through a small wetland.

1.6. Methods applied to study metal sources, behaviour and bioavailability

The study of metal contamination in rivers requires the measurement of different parameters *in situ* and *ex situ* and the use of multiple techniques. To understand the underlying conditions determining behaviour and fate of metals, the *in situ* parameters to be measured should include pH, water temperature, dissolved oxygen, water conductivity, turbidity, flow, major ions, dissolved organic carbon and free metal ions (Nieto et al., 2007; Mohiuddin et al., 2010).

With regard to free metal ions they typically represent a minor component of total metal species. These ions form complexes with inorganic and organic ligands

showing different physical properties, such as charge, size, and diffusion coefficient. The formation of these ion-complexes in natural waters can have a major effect on the rates of redox processes, mineral solubility and biochemical availability (Li et al., 2005). These forms of metal can be measured using *in situ* devices such as ion-selective electrodes (ISE) consisting of a reference electrode, ion-selective membrane and voltmeter for determining the concentrations of various cations and anions in aqueous solutions, and the Donnan membrane techniques (DMT) that use an exchange membrane to measure free ion concentrations based on the principle of the Donnan membrane equilibrium (Temminghoff et al., 2000; Di Toro et al., 2001). In the 1990s a novel technique was developed called Diffusive Gradient in Thin films (DGT) which has been applied to measure the contaminant levels in several river ecosystems. DGT has the advantages of being a multi-element method and providing a time-averaged concentration (Han et al., 2013). This method is considered a robust *in situ* monitoring tool for labile metal species. It provides information of solute concentrations and their dynamics (mobility and kinetics) in sediments, soils and water (Davison and Zhang, 1994; Zhang et al., 1998; Zhang, 2004; Zhang and Davison, 2015). For accumulating metals DGT employs a three-layer system consisting of: i) a Chelex resin-impregnated hydrogel layer; ii) a polyacrylamide hydrogel diffusion-layer; and iii) a filter membrane. The Chelex resin is selective for inorganic metal species and provides a labile fraction of pre-concentrated metals in solution (Zhang and Davison, 1995) (Figure 1.5).

Water passes through the filter membrane (pore size = 0.45 μm) which protects the fragile polyacrylamide layers and isolates them from particulate matter. Metal species in water are transported through the diffusion boundary layer (DBL) and the diffusive gel. Finally, the Chelex resin gel (a strong metal complexing agent) serves as a sink for labile inorganic metal species (Zhang and Davison, 2000). After retrieval this resin is removed for mass analysis of metals. Metal concentrations can be calculated using the equation shown in figure 1.6.

In relation to *ex situ* parameters one of the most important is the measurement of chemical metal forms (total, dissolved and particulate). This measurement is frequently performed using a Thermal Ionization Mass Spectrometry (TIMS) or

Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) both of which identify major trace metals (Becker and Dietze, 1998).

Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) has been widely used over the years in a number of different fields including analyses of drinking water, of wastewater, of natural water systems, in hydrogeology, geology and soil science, mining/metallurgy, food sciences, and medicine (Montaser, 1998; Moens, 1997; Panday et al., 1996; Pröfrock and Prange, 2012). This technique has the ability to carry out rapid multi-element determinations at ultra-trace level for a wide variety of elements (Brown and Milton, 2005). It separates ions according to their mass and from their charge ratio calculates ion concentrations. All elements can be simultaneously analysed quickly (seconds) and low limits can be detected (Greenfield et al., 1992). The system comprises five basic steps: i) generation of an aerosol from the sample, ii) ionization of the sample in the inductively couple plasma source, iii) extraction of ions from the sampling interface, iv) separation of ions according their mass, and v) detection of ions and calculating metal concentrations (Figure 1.7).

In addition, other chemical measurements are applied for the better understanding of metal mobility and toxicity. For example, the analysis of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) provide the amount of carbon species in solution by using the Total Carbon Analyzer. Cation-anion analysis is commonly performed by Ion Chromatography which has been approved by many standard or regulatory organizations in numerous countries for testing environmental samples (EPA, 1997).

a) b)

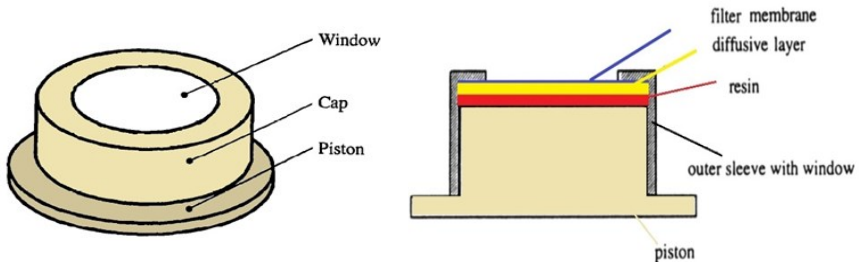

Figure 1. 5. Schematic representation of a DGT device: (a) parts of a device and (b) sections through the device: i) Resin: Chelex resin, ii) Diffusive layer: polyacrylamide hydrogel, and iii) Filter membrane (Zhang and Davison, 1995).

Equation(1)

$$C_{DGT} = m\Delta g/DAt$$

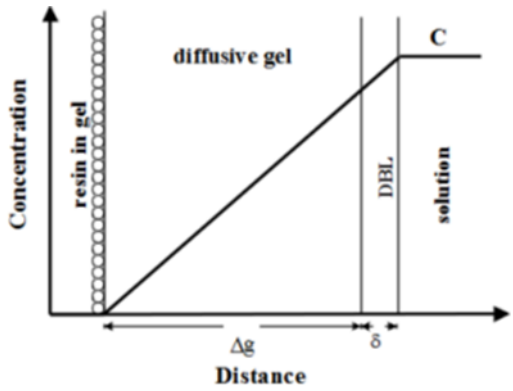

Figure 1. 6. Equation for quantification of metal concentrations. Where *m* is the mass on the resin gel, *Δg* is the thickness of the diffusion gel, *D* is the diffusivity of metal ions through the gel, *A* is the surface area of the gel, and *t* is the total time deployed. From Zhang and Davison (1995).

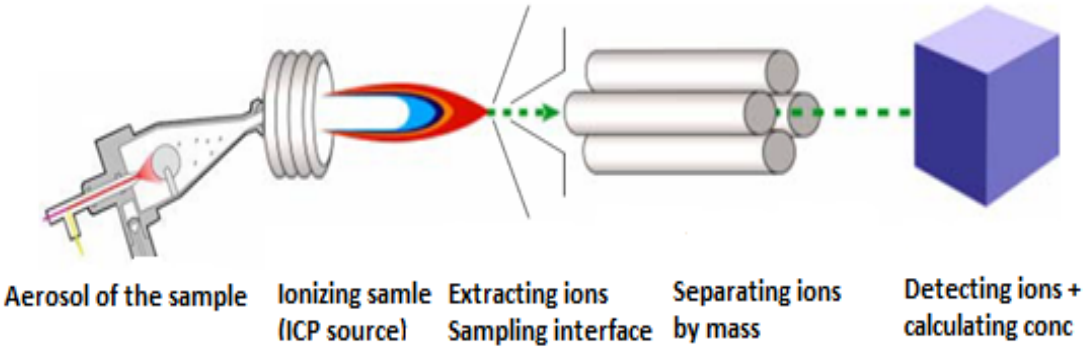

Figure 1. 7. Scheme of the analytical phases in ICP-MS (*Source: http://www.thermo.com).*

The growing interest in the ability to anticipate pollution scenarios and design management strategies for the minimisation of environmental impact have resulted in the development of several models (e.g. PHREEQC, BLM, WHAM). For instance, PHREEQC (Parkhurst and Appelo, 1999) is a geochemical model that simulates a variety of geochemical processes including equilibrium between water and minerals, ion exchangers, surface complexes, solid solutions, and gases. The general formulation allows modelling of non-equilibrium mineral dissolution and precipitation, microbial reactions, decomposition of organic compounds, and other kinetic reactions (Charlton and Parkhurst, 2011). This geochemical modelling has been applied in several fields, including environmental protection and remediation (Caruso et al., 2008; Obiri-Nyarko et al., 2015). Speciation models estimate element distributions on the basis of known or postulated chemical reactions (Turner, 1995). The Biotic Ligand Model (BLM) postulates a single binding site of toxic action (the biotic ligand). BLM depends on the site-specific water quality including parameters such as pH, temperature and organic-inorganic complexes with other abiotic factors such as cationic competition (e.g., Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}) (Di Toro et al., 2001; Heijerick et al., 2002) (Figure 1.8).

Over the last years, BLM has been focus of extensive technical reviews and laboratory tests due to its applicability in the regulatory framework (Santore et al., 2001; Niyogi and Wood, 2004). The BLM has contributed to the improvement of metal Environmental Quality Standards (EQS) estimated from total metal concentrations and laboratory toxicity data (when field situations are poorly representative) for chemical and ecological assessment. The BLM provided relevant measurements of metal risk, reducing background concentrations, toxicity of metal forms and the specific metal response to water quality (e.g. The Netherlands 2004, Denmark 2007). The US Environmental Protection Agency has used this model to outline Ambient Water Quality Criteria (AWQC) in surface water and to revise freshwater acute criterion (e.g. Cu BLM) (EPA, 2007). Equally, the UK Environment Agency has tested the use of BLMs within a regulatory framework, offering a practical approach for assessing metal bioavailability (e.g. metal bioavailability assessment tools, M-BATs). Moreover,

groups from the metal industry have also adopted this tool to accompany existing substances regulations (793/93/EEC) (Johnston et al., 2008).

Many analytical techniques are available but rarely can determine a complete metal species distribution. Over the years, speciation models have been improved to estimate the metal forms that are bioavailable in freshwaters and soils (Lofts and Tipping, 2011; Pérez-Esteban et al., 2014; Farley et al., 2015). Furthermore, humic substances are recognized to have an important role in metal speciation (Tipping, 1994). These substances are produced by biodegradation of organic matter and they can be divided into three main fractions: humic acids (HA), fulvic acids (FA), and humin (Hessen and Tranvik, 2013). Generally, they have the ability to form chelate complexes with ions such as Mg^{2+}, Ca^{2+}, Fe^{2+} and Fe^{3+}. Chelate complexes are important factors for regulating metal ion bioavailability.

Geochemical speciation models have been upgraded for aquatic environments dominated by humic substances. In this respect, the Non-Ideal Competitive Adsorption (NICA) coupled with a Donnan electrostatic sub-model uses a continuous distribution approach to describe metal and proton bindings to organic matter (Benedetti et al., 1995; Kalis et al., 2006). Additionally, the programme called Windermere Humic Aqueous Model (WHAM) is based on two components: i) the Humic Ion-Binding Model established by interactions of protons and metals with natural organic matter and ii) other models based on mineral oxides, inorganic solution chemistry, cation-exchange and fulvic acid reactions (Tipping and Hurley, 1992). To calculate metal speciation WHAM assumes thermodynamic and chemical equilibrium and uses a number of water chemistry parameters (e.g. pH, dissolved organic carbon-DOC, cation concentrations, and anion concentrations) (Tipping, 1994).

The original version of WHAM has been improved in recent years. The latest was the inclusion of a wider range of parameterised data obtained from studies on metal binding to humic and fulvic acid isolations into the Humic Ion-Binding Model section (Tipping, 2005; Tipping et al., 1998; Tipping and Carter, 2011). From this advanced dataset, WHAM offers the possibility to close the gap between laboratory experiments, field observations and the long-term reactions (i.e.

months or years) for predicting chemical speciation and key interactions in field situations, and optimising remediation efforts. In this context, the WHAM model has been widely used on studies related to soil solution, ground and surface water acidification, trace metal behaviour, lake sediment diagenesis, rare earth geochemistry, organic matter solubility, catchment modelling, metal interactions with biota, ecotoxicology and critical loads (Hamilton-Taylor et al., 1997; Ferreira et al., 1997; Cheng et al., 2005; Tipping et al., 2006a; 2006b).

Furthermore, the suitability of WHAM offers a relevant approach in research and regulatory areas. In the UK, previous versions of WHAM have been critical in the development of BLMs for predicting the toxicity of metals to aquatic organisms (e.g. BLM for Copper, Zinc, Nickel and Manganese) (Merrington and Peters, 2013). However, BLMs have limitations for assessing metal mixtures effects as BLMs are based on specific metal-organism interactions, without including all dissolved forms of metals. To tackle this restriction, WHAM-F_{TOX} is an alternative bioavailability-based model for quantifying mixture toxicity and potential effects on aquatic organisms (Stockdale et al., 2010) (Figure 1.9). WHAM-F_{TOX} has been applied in several studies for predicting metal toxicity to aquatic biota (e.g. freshwater macroinvertebrates and zooplankton species) (Tipping and Lofts, 2013; 2015; Stockdale et al., 2010; 2014; Qiu et al., 2015).

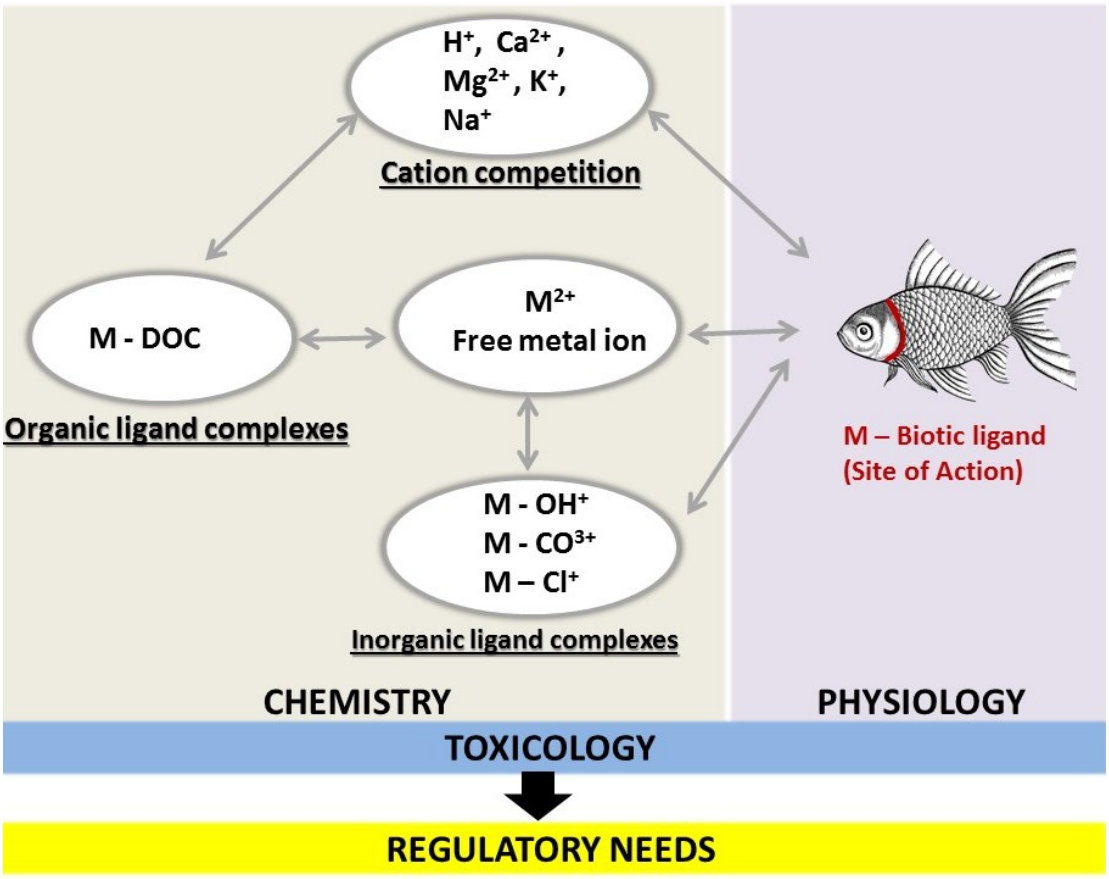

Figure 1. 8. Schematic of BLM presenting chemistry, physiology and toxicology. Modified from Paquin et al. (2002).

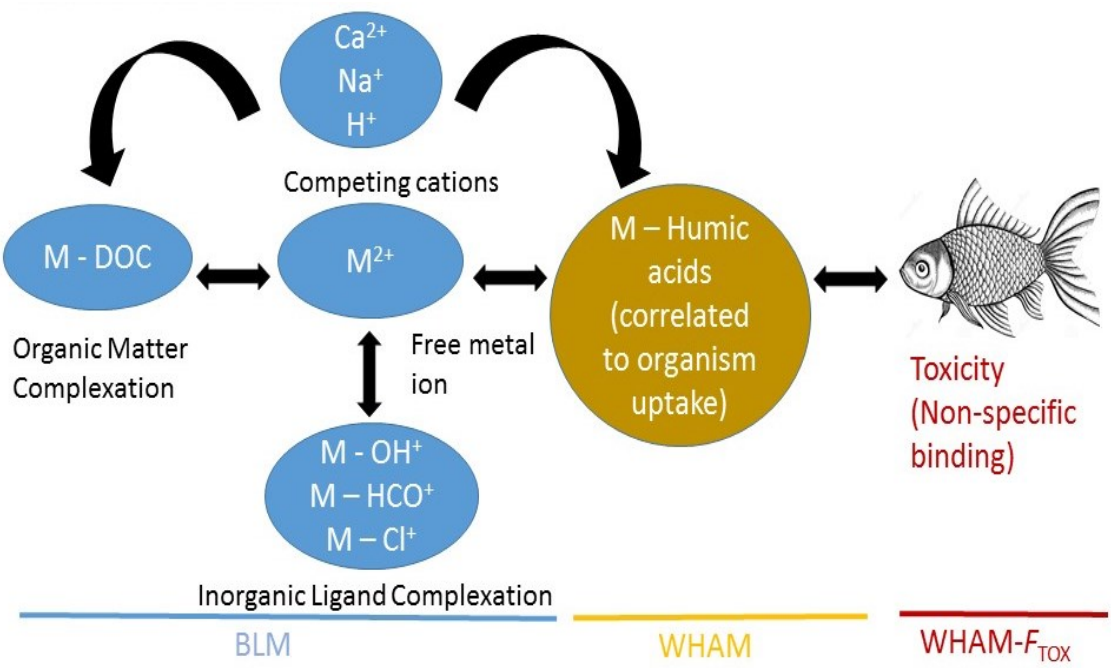

Figure 1. 9. Principles used by BLM, WHAM and WHAM-F_{TOX}. Modified from Di Toro et al. (2001).

1.7. Metal remediation in freshwater

Metal remediation depends on site characteristics such as: concentration, pollutants forms, contaminated medium and resource end use (Mulligan et al., 2001). Mine water treatment technologies have been reviewed extensively (Brown et al., 2002; Lottermoser, 2010; Younger, 2000). Remediation methodologies for mine water can be categorized generally into active and passive treatment. Active technologies use electrical energy and mechanized procedures requiring constant monitoring and maintenance (Jarvis et al., 2007). Passive systems use natural energy such as topographical gradient, metabolic energy and photosynthesis to drive remediation processes, reducing operation and maintenance costs (Pulles and Heath, 2009). Thus, passive techniques such as ion-exchange, adsorption, precipitation and membrane filtration are frequently used for the removal of heavy metal from wastewater (Barakat, 2011; Younger, 1998).

Metal contaminants released from mining and processing operations and entering river systems have given rise to remediation problems. Long-term metal contamination of bed and floodplain sediments affect the river water quality over extensive distances (Ciszewski et al., 2012). Thus, in recent years, methods for heavy metal remediation have been performed based on water quality understanding and by integrating ecological processes. Ultimately, the selection of the most suitable techniques depends on availability of capital investment, functioning costs, design flexibility, reliability and environmental impacts (Fu and Wang, 2011; Birch, 2011).

In the UK, various remedial technologies have been trialled for circumneutral metal mine drainage (pH from 5.5 to 7.4) (Nuttall and Younger, 2000; Younger, 2000; Mayes et al., 2009a; Jarvis, 2014). However, remediation measures in historical mining areas are still a challenge. One full-scale mine water treatment plant has been built at the Wheal Jane tin mine in Cornwall which was abandoned in 1992. Additionally, in the Lake District experts have designed a vertical flow pond, which uses compost and limestone to treat metal-rich water from an ancient mine called Force Crag. Other pilot-scale treatments have been built in Wales,

Cornwall and the North Pennines to assess the feasibility of treatment by different methods (Johnson and Hallberg, 2005; Johnston et al., 2008).

In Hebden Beck, the presence of extensive tailings turns the diffuse metal pollution in a major issue particularly under higher flow (Jones et al., 2013). Passive remediation has been suggested as a potential approach for this catchment (Baxter, 2015). However, in conservation areas, remediation systems fail the challenge of how to achieve a balance between water quality improvements, the protection of endemic metal-tolerant species and the conservation of historic structures with archaeological significance (Potter et al., 2004; Rolston et al., 2017). Thus, mining remediation schemes offer the opportunity to involve technical experts and the community. Through this integration, local engagement will be encouraged by understanding basic metal mitigation approaches and will motivate the protection of remediation structures (Tindale, 2014; Hu, 2011; DEFRA, 2013).

1.8. Site selection process

Sites were selected from the most mining impacted area, covering approximately 5 km^2 of Hebden catchment (12 km long) including point and diffuse sources flowing downstream from mine sites (Figure 1.10). Sixteen sampling sites were chosen for water sampling representing the main channel, minor and major tributaries, and a source pool feeding a tributary. Eight of these sites (about 3.3 km) were part of a water quality monitoring programme conducted by the Environment Agency (Barber, 2014). The other eleven sites were selected based on their proximity to mine wastes (e.g. tailings and spoils) (Table 1.5). Monthly sampling campaigns were carried out from November 2013 to December 2014.

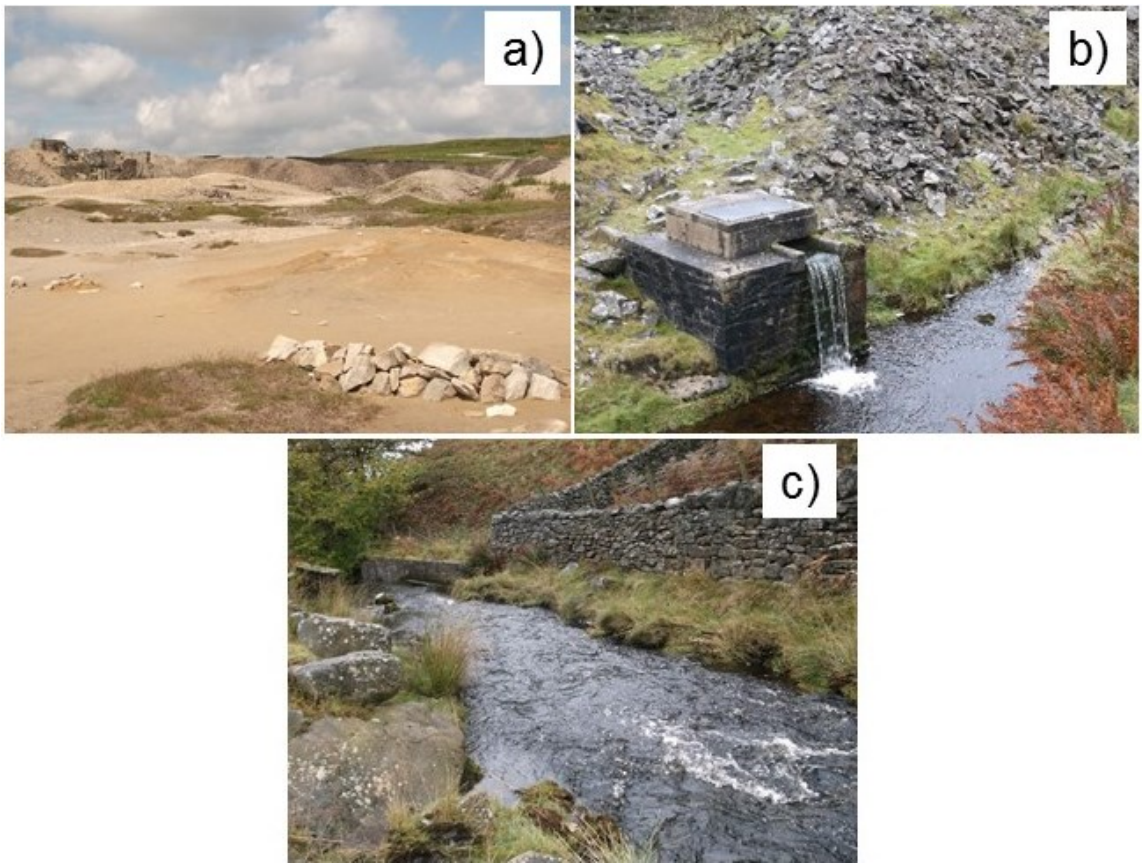

Figure 1. 10. Main catchment features. Panel a, represents diffuse source of metal pollution (ephemeral tributary). Panel b, corresponds to a point source. Panel c represents the main channel.

Table 1. 5. Sampling sites along Hebden Beck. Table indicates type of sample, site elevation, coordinates, and distance from River Wharfe. Sites are listed from upstream to downstream. Locations adopted from the Environment Agency monitoring programme are indicated with (*).

Site ID	Site Description	Type of sample	Elev.	Coordinates		From R. Wharfe (m)
			(m)	East	North	
H15	Head water reservoir (Next-smelt mill)	Water	368	402798	466766	4970
GM	Grassington moor, spoil wastes	Spoil	380	403014	466663	
H14	Perennial tributary (Coalgrove Beck)	water, sediment	294	402413	466106	4207
H13	Ephemeral tributary	Water	287	402443	465931	4030
B1	Beaver, spoil wastes (from heap)	Spoil	320	402087	465660	
B2	Beaver, spoil wastes (silt runoff)	Spoil	317	402163	465630	
H12	Ephemeral tributary (downstream-Yarnbury mine-Beaver spoil)	water, sediment	285	402451	465822	3921
H11	Perennial tributary (Loss Gill Dike)	Water	278	402597	465578	3637
H10*	Main channel	water, sediment	267	402656	465324	3377
H9*	Perennial tributary (Bolton Gill)	Water	266	402661	465285	3338
H8*	Ephemeral tributary (from-Yarnbury mine)	Water	268	402632	465176	3226
H7*	Perennial tributary (Adit) – Bolton Haw	Water	266	402648	465164	3206
H6*	Main channel	Water	257	402630	464916	2958
H5*	Perennial tributary (Duke's adit)	Water	256	402638	464793	2836
H4	Ephemeral tributary (Waterfall)	Water	254	402668	464604	2645
H3*	Perennial tributary (Laneshaw adit)	Water	246	402632	464550	2580
H2*	Main channel at gauging station	Water	235	402488	464275	2271
H1P	Perennial tributary	water	233	402382	464104	2071
H1	Main channel - Confluence R. Wharfe	water, sediment	152	402695	462400	140

1.9. Aim and specific objectives

The overall aim of this research is to assess metal contamination derived from historical mining by evaluating sources, mobility and toxicity in river to support management strategies for improving water quality status. Specific objectives are formulated below.

- Understand how geochemical processes control the concentration and mobility of dissolved metals in neutral-rich drainage.
- Evaluate metal speciation and potential bioavailability to determine ecotoxicological risk.
- Examine the effects of episodic rainfall events on metal fluxes and any consequential effects on ecotoxicity.
- Assess the public perception about water quality of Hebden Beck.

1.10. Thesis Outline

In Chapter 2, I have characterized the metal pollution of the Hebden catchment. Using mineralogical analysis and geochemical modelling, mineral sources controlling weathering reactions and metal mobility were identified. Key chemical relationships in neutral mine drainage were identified. Furthermore, the effect of seasonal trends in metal concentrations were evaluated.

In Chapter 3, I assessed the distribution of different metal forms and interactions with organic and inorganic compounds, including toxic effects to organisms. In addition, I evaluated current metal assessment techniques using water chemistry, together with speciation and toxicological predictions for assessing river water quality and ecotoxicological effects. This appraisal supported the use of bioavailability-based approaches and their applicability for future metal risk assessments.

In Chapter 4, I evaluated the effects of episodic rainfall in catchments with historical metal mining areas. These events might produce metal-rich runoff having greater impacts on river water quality than base flow. Here I provide a timely analysis of the water chemistry and processes associated with deposition and remobilisation of metals during episodic rainfall events. These findings could

be applied in the assessment of streams draining other spoil waste areas with similar geochemical conditions and inform future management strategies.

In Chapter 5, I appraised the public perception (residents, visitors and stakeholders-regulator) of the river water quality of Hebden Beck. In addition, I explored public views about potential remediation techniques. The results reflected the deficient translation of technical knowledge from regulators to the public. Regarding remediation approaches, this study was focused on public perceptions rather than operational aspects, thus outcomes could provide an insight into preferred remediation techniques and a local involvement in the protection of the river ecosystem.

In Chapter 6, the main findings from chapters 2–5 are drawn together and discussed. This section contains further in-depth critical analysis of the results and places them in the context of the literature. Finally, the overall conclusions from the thesis are summarised.

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Chapter 2: Understanding the mobilisation of metal pollution associated with historical mining in a carboniferous upland catchment

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Abstract

Point and diffuse pollution from metal mining has led to severe environmental damage worldwide. Mine drainage is a significant problem for riverine ecosystems, it is commonly acidic (AMD), but neutral mine drainage (NMD) can also occur. A representative environment for studying metal pollution from NMD is provided by Carboniferous catchments characterised by a circumneutral pH and high concentrations of carbonates, supporting the formation of secondary metal-minerals as potential sinks of metals. The present study focuses on understanding the mobility of metal pollution associated with historical mining in a Carboniferous upland catchment. In the uplands of the UK, river water, sediments and spoil wastes were collected over a period of fourteen months, samples were chemically analysed to identify the main metal sources and their relationships with geological and hydrological factors. Correlation tests and principal component analysis suggest that the underlying limestone bedrock controls pH and weathering reactions. Significant metal concentrations from mining activities were measured for zinc (4.3 mg/l), and lead (0.3 mg/l), attributed to processes such as oxidation of mined ores (e.g. sphalerite, galena) or dissolution of precipitated secondary metal-minerals (e.g. cerussite, smithsonite).

Zinc and lead mobility indicated strong dependence on biogeochemistry and hydrological conditions (e.g. pH and flow) at specific locations in the catchment. Annual loads of zinc and lead (2.9 and 0.2 tonnes/year) demonstrate a significant source of both metals to downstream river reaches. Metal pollution results in a large area of catchment having a depleted chemical status with likely effects on the aquatic ecology. This study provides an improved understanding of geological and hydrological processes controlling water chemistry, which is critical to assessing metal sources and mobilization, especially in neutral mine drainage areas.

2.1. Introduction

Anthropogenic activities have become an important driver of the global biogeochemical cycling of metals. Present day and historical mining have caused the release of heavy metals into fluvial environments. Globally, pollution from metal mining has led to severe damage to riverine ecosystems in many catchments (Horowitz et al., 1993; Macklin, 1996; Hudson-Edwards et al., 1999; Nagorski et al., 2002; Miller et al., 2004; Fernandes et al., 2016). In the United Kingdom, old mines from the 18th and 19th centuries represent the major diffuse source of metals having an adverse effect on aquatic ecosystems (Macklin, 1997; Hudson-Edwards, 2003; Olías et al., 2004; Oulton et al., 2014). Rivers draining these mining areas are heavily affected by metal pollution as mineral veins present elevated concentrations of lead and zinc ores with variable concentrations of cadmium, barium and fluorine (Hudson-Edwards et al., 1997).

Water chemistry in surface waters are particularly vulnerable to biogeochemical and hydrological processes which are controlled by seasonality (Warren and Haack, 2001; Byrne et al., 2012; Jones et al., 2013). In this context, knowledge about metal mobility in natural water systems is extremely complex (Luoma, 2008). Biogeochemical partitioning of metals results in a diversity of forms. Within the dissolved phase metals are present as hydrated free ions, and associated with organic and inorganic complexes. Within the suspended particulate phase, metals may be complexed with inorganic or organic particles and biota or be present as discrete metal minerals. Adsorption and desorption of metals depend

on a number of factors including pH, redox conditions, mineral ore sources and the composition of suspended particulate matter. For this reason, developing an improved understanding of the mechanisms determining the mobility and toxicity of metals within aquatic ecosystems is a key issue, which can in turn support efforts to manage or mitigate pollution (Elder, 1988).

Several countries have developed guidelines to obtain good ecological and chemical status of and ground waters (Apitz et al., 2006). In the European Union (EU), the implementation of the Water Framework Directive (WFD) obliges member states to assess surface waters through improved catchment scale management (River Basin Management Plans, RBMPs). However, surface water bodies such as headwater streams have been excluded from early RBMPs due to their small size. Studies from Freeman et al. (2007), Dodds and Oakes (2008), and Meyer et al. (2007) have shown the importance of these waterbodies as biodiversity richness, migration corridors, origin of stream networks and diffuse source of chemicals. Consequently, sound management is crucial for maintaining ecosystem health in higher order streams that are targeted by the WFD aims.

A serious environmental hazard caused by mining is the generation of acid mine drainage (AMD). Mine drainages, spoil wastes run-off and spoil erosion constantly discharge large amounts of dissolved and particulate metals through AMD, representing a persistent and acute pollution source and reducing water and sediment quality (Mayes et al., 2009; Byrne et al., 2012; Jones et al., 2013). Studies of mine wastes chemistry have identified two types of mine effluents, acid mine drainage (low pH and high concentration of dissolved sulphate) and circumneutral mine drainage (major ion concentrations reflect the mineralogy of the catchment bedrock) (Banks et al., 2002; Akcil and Koldas, 2006). Thus, mine drainage is dependent on the geologic setting, local water chemistry, kinetic rates, and permeability of ore and gangue minerals (Navarro et al., 2015; Plumlee et al., 1999; Cravotta Iii, 2008a; Cravotta Iii, 2008b; Sánchez España et al., 2005). Mine drainage flowing through Carboniferous limestone host rock is consequently metal-rich but with a circumneutral pH (Byrne et al., 2012; Jones et al., 2013). Research from Lindsay et al. (2009) and Desbarats and Dirom (2007) indicates that circumneutral mine drainage might support natural attenuation of some

metal-sulphides (e.g. ZnS, PbS) through the precipitation of secondary minerals. Consequently, catchments under these conditions may be more vulnerable to environmental harm due to changes in geochemical or hydrological conditions, producing high pulses of dissolved metal concentrations or long leaching processes in response to decades of chemical weathering (Heikkinen et al., 2009; Lottermoser, 2010).

Another long-standing metal pollution problem is physical and chemical mobilisation of metals through the passive dispersal and active transformation of abandoned tailings, spoil heaps, bed sediments and contaminated floodplains. Studies on metal transportation from mine wastes have reported the mobility of metals over long distances as free ions and complexed forms within rivers. In addition, solid phases can be stored within floodplain deposits for decades to millennia (Miller, 1997; Gosar et al., 1997; Hudson-Edwards, 2003; Hudson-Edwards et al., 2005; Cave et al., 2005; Taylor and Hudson-Edwards, 2008). In an area of the UK with Carboniferous bedrock, the north Pennines, historical metal mining has directly affected surface and subsurface floodplain soils with heavy metal concentrations above background levels (Johnston et al., 2008). Specifically, the Yorkshire Ouse basin which drains the Pennine Orefield is estimated to contain 620 million tonnes of lead and 640 million tonnes of zinc stored within its floodplains (Hudson-Edwards et al., 1999). Given the large differences in chemistry between acid and circumneutral mine drainage, particularly in the concentrations of protons and of Fe and Al whose solubility is controlled by pH, there will be significant differences in the degree of availability of metal forms that can interact with aquatic organisms. This necessitates dedicated studies of such Carboniferous catchments.

This study aims to understand metal occurrence and mobilisation in a Carboniferous limestone upland catchment impacted by former lead and zinc mining. Comprehensive water monitoring and analysis of sediment and spoil samples are used to describe the effects of historical mining on a whole small river catchment in the northern Pennines region of North Yorkshire, UK. We sought to provide a better understanding of how geochemical processes control the concentration and mobility of dissolved metals in neutral metal-rich drainage.

The results have wider implications for management strategies of potential environmental harm in such catchments.

2.2. Site characteristics of Hebden Beck

2.2.1. Lithology and geology

Hebden Beck is a sub-catchment of the River Wharfe located in the northern Pennines region of the United Kingdom and within the Yorkshire Dales National Park. Hebden Beck rises from Grassington Moor and is joined by multiple tributaries including Coalgrove Beck, Bolton Gill and Loss Gill before the confluence with the Wharfe. It is approximately 12 km long, with the upper reach (6.4 km) of the main channel being the most heavily impacted by historic mine working. It drains an area of 26 km^2 and subsequently flows into the River Wharfe which drains the Wharfedale valley. The Wharfe flows into the River Ouse and ultimately reaches the sea at the Humber Estuary which is one of the largest in the UK (24,750 km^2). The geology of Hebden Beck is dominated by Millstone Grit sandstone (approx. 20 km^2) but crucially also contains bands of Carboniferous limestone (approx. 6 km^2) (Figure 2.1). The catchment cover comprises 46% peatlands, predominantly in the upstream areas, 35% Carboniferous limestone, mainly in the south and 19% glacial sediment, predominantly in the west (Barber, 2014).

2.2.2. Ore processing and mine wastes

Hebden's orefield comprised coal and lead-zinc mineral deposits, where galena (PbS) is the most common mineral, but with associated sphalerite (ZnS), chalcopyrite ($CuFeS_2$), barite ($BaSO_4$), fluorite (CaF_2) calcite ($CaCO_3$) and witherite ($BaCO_3$) (Barber, 2014). These minerals occur mostly in vertical veins along fault planes. Early mine workings were open cuts and shafts to extract deeper layers of lead ore. In later years until around 1850, the hushing method was used to scour away the soil using the erosive power of water to expose mineral veins. This method required the construction of dams to control streams, and manmade channels to divert water. Horizontal drainage levels (adits) were

driven from the valley bottoms to enable deeper working and easier removal of minerals. Lead ores were crushed, classified and bagged at the dressing floors located at the surface close to the mines, then transported to the smelting mills to be processed. Water power was also applied at the dressing floors and smelt mills, therefore spoil tips or mine wastes are located next to rivers. Approximately, 124 mining features exist in the Hebden Beck catchment area, however main features are 5 lead-zinc mines, 15 adits, 7 spoil tips and 4 smelters. From 1700-1900, 1686.5 tonnes of lead were extracted from these mines (Gill, 1993).

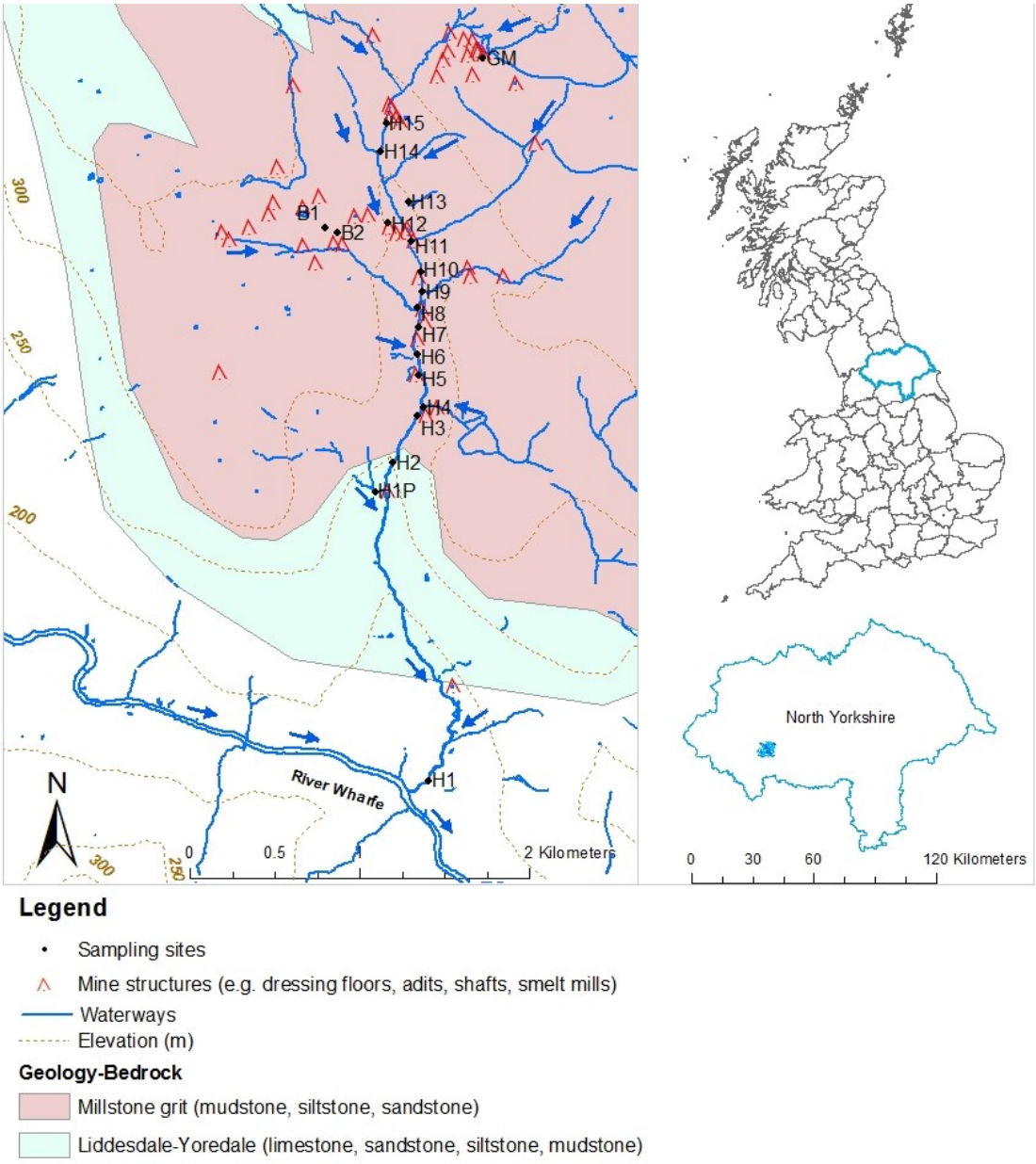

Figure 2. 1. Hebden Beck with sampling sites and mine structures located in the Millstone grit and Liddesdale-Yoredale bedrock. Blue arrows indicate the direction of flow.

2.3. Methods

2.3.1. Sampling strategy

Sites were selected from the most impacted area, covering an area of 5 km^2 including point and diffuse sources flowing downstream from mine sites. A total of sixteen sites were chosen for water sampling including the main channel, minor and major tributaries, together with a source pool feeding a tributary (Table 2.1). Eight of these sites (about 3.3 km) were part of a water quality monitoring programme performed by the Environment Agency (Barber, 2014). The other eleven sites were selected based on their proximity to mine wastes (e.g. tailings, spoils). Monthly sampling campaigns were carried out from November 2013 to December 2014.

2.3.2. Water sampling

Samples were taken from downstream to upstream (H1 to H15) in order to minimise contamination of other sites by disturbance (APHA, 1995). At each site, a sample was taken with a pre acid washed (10% HNO_3, Nitric acid-Sigma Aldrich 69% and Milli-Q water) 750 ml polypropylene bottle attached to a plastic pole. Four subsamples were then extracted from this bottle. For total metals, unfiltered samples were placed individually into a pre-weighted 50 ml tube (polypropylene) containing 1 ml of preservation solution (10% HNO_3) to reach 1% v/v of the final volume and pH ≤ 2 (Apha, 1995; US Environmental Protection Agency and Office of Research and Development, 1982). For dissolved metals analysis, samples filtered through syringe filters (0.45 μm, polyethersulfone-hydrophillic, Sartorius) were placed individually into a pre-weighted 50 ml tube (polypropylene). Then preservation solution (10% HNO_3) was added as used for total metals. For quantifying major anions, the sample was filtered (Sartorius syringe filters 0.45 μm, polyethersulfone-hidrophillic) and placed into polypropylene tubes. For inorganic and organic carbon analysis the samples were passed through syringe filters (0.45 μm, nylon-polypropylene, Avonchem) and placed into polypropylene tubes. All samples were kept in a cool box during sampling and transported the same day to the laboratory for storage. Samples for major anions analysis were

stored frozen at -20°C, while samples for all other analyses were refrigerated at 4°C.

A carbon Analyser (Analytik Jena Multi N/C2100) was used for measuring carbon compounds (dissolved inorganic carbon-DIC and dissolved organic carbon-DOC), Ion Chromatographer for major cations (Ca, Mg) and anions (Cl^-, NO_3^-, SO_4^{2-}) (Dionex ICS-3000), and SEAL Analytical AA3 was used for orthophosphate quantification. For metal analysis, nine elements were measured (Pb, Ba, Cd, Sr, Zn, Cu, Fe, Mn, Al), using inductively coupled plasma mass spectrometry (ICP-MS; Thermo Fisher iCAPQc) with specific limits of detection (Pb: 0.01 μg/l, Ba: 0.06 μg/l, Cd: 0.01 μg/l, Sr: 0.08 μg/l, Zn: 67 μg/l, Cu: 0.05 μg/l, Fe: 0.11 μg/l, Mn: 0.04 μg/l, Al: 0.16 μg/l). Field blanks (n= 3) and replicates (n= 3) were collected at each sampling campaign.

2.3.3. Sediment and spoil sampling

Most sites were dominated by large rocks and coarse sediment. Sediment samples were collected during a single campaign at specific sites (H14, H12, H10 and H1) to assess the evolution of mineral composition. Plastic scoops were used for their collection by wading along a cross-section of the stream. Sediments were sieved through a <250 μm stainless steel mesh and transferred into 50ml polypropylene tubes. Spoil sampling was carried out at single spoil heaps at Grassington Moor (GM) and the Beaver spoil area (B1), in addition a further sample was collected at the Beaver spoil area that represented material that had been subjected to movement and size sorting by the actions of rainfall events (B2).

In the laboratory, sediment samples were centrifuged at 3200 rpm for 10 mins to allow removal of the supernatant. The supernatant was decanted and the resulting slurries were placed in a petri dish to air dry. After drying, sediments were placed into zip log bags for disaggregation. Spoil samples (B1, B2, and GM) were dried to calculate percentage water composition. The surface area was also measured to estimate the mineral area available for dissolution reactions. This was performed using the Brunauer, Emmett and Teller method (BET; Micromeritics Gemini VII 2390a) on 2 g of sample dried overnight under N_2 gas at 75 °C. In addition, both sediment and spoil samples were analysed by X-ray

Diffraction (XRD, Bruker D8-Discover instrument) for determining mineralogy of the major constituents and X-ray Fluorescence (XRF, Innovex X-5000) for chemical composition. The minimum mineral fractions required for detection on this instrument is 2-3%. The standard reference material STSD-3 (stream sediment) was used as XRF quality control.

2.3.4. In situ measurements

Pre-calibrated multiple sensor probes (Model HQ30d flexi 1032) were used in the field to measure pH, dissolved oxygen (DO: mg/l) and conductivity (EC: μS/cm). Flow rate (m^3/s) was calculated from *in situ* flow velocity measurements (m/s) (flow meter: Global 800-876) together with data from river depth (m) and width (m). Flow data from the UK Environment Agency gauging station (H2) was also obtained from their continuous monitoring records. This flow data together with metal concentrations were used for the calculation of annual metal loading and comparison with Environmental quality standards (EQS) for freshwater in the UK (Barber, 2014).

Table 2. 1. Sampling sites along Hebden Beck. Table indicates type of sample, site elevation, coordinates, and distance from River Wharfe. Sites are listed from upstream to downstream. Locations adopted from the Environment Agency monitoring programme are indicated with (*).

Site ID	Site Description	Type of sample	Elev. (m)	Coordinates East	Coordinates North	From R. Wharfe (m)
H15	Head water reservoir (Next-smelt mill)	Water	368	402798	466766	4970
GM	Grassington moor, spoil wastes	Spoil	380	403014	466663	
H14	Perennial tributary (Coalgrove Beck)	water, sediment	294	402413	466106	4207
H13	Ephemeral tributary	Water	287	402443	465931	4030
B1	Beaver, spoil wastes (from heap)	Spoil	320	402087	465660	
B2	Beaver, spoil wastes (silt runoff)	Spoil	317	402163	465630	
H12	Ephemeral tributary (downstream-Yarnbury mine-Beaver spoil)	water, sediment	285	402451	465822	3921
H11	Perennial tributary (Loss Gill Dike)	Water	278	402597	465578	3637
H10*	Main channel	water, sediment	267	402656	465324	3377
H9*	Perennial tributary (Bolton Gill)	Water	266	402661	465285	3338
H8*	Ephemeral tributary (from-Yarnbury mine)	Water	268	402632	465176	3226
H7*	Perennial tributary (Adit) – Bolton Haw	Water	266	402648	465164	3206
H6*	Main channel	Water	257	402630	464916	2958
H5*	Perennial tributary (Duke's adit)	Water	256	402638	464793	2836
H4	Ephemeral tributary (Waterfall)	Water	254	402668	464604	2645
H3*	Perennial tributary (Laneshaw adit)	Water	246	402632	464550	2580
H2*	Main channel at gauging station	Water	235	402488	464275	2271
H1P	Perennial tributary	water	233	402382	464104	2071
H1	Main channel - Confluence R. Wharfe	water, sediment	152	402695	462400	140

2.3.5. Data analysis

Geochemical modelling

The PHREEQC code (version 3) (U.S. Geological Survey (USGS); Parkhurst and Appelo, 1999) was used for modelling main geochemical reactions occurring in aqueous solutions. This software allows the prediction of mineral precipitation that potentially controls the composition of the aqueous phase. Equilibrium reactions and thermodynamic constants were retrieved from the built-in WATEQ4F database (Nordstrom et al., 1990; Ball and Nordstrom, 1991; Drever, 1997). Mineral saturation indices and metal free ion activities for hydroxide, carbonate and sulphate minerals were calculated for the pH range 3.5-9 and based on mean values across our field sites and all sampling dates: temperature 10 °C, SO_4^{2-} ($\bar{x}$: 13592 μg/l) and Cl^- ($\bar{x}$: 7730 μg/l). With calculations for carbonate minerals the pCO_2 was fixed at three times the atmospheric concentration (0.0012 atm), consistent with typical supersaturation of this gas in streams. These model predictions are compared with metal free ion activities calculated for each sampling site and date to investigate the controlling mineral phases.

Principal Component Analysis

Principal component analysis (PCA) was conducted to identify the main factors influencing metal distribution. Linear correlation analysis was applied to evaluate the relationships among the studied metals, other compounds and *in situ* parameters. Results of Pearson and Spearman tests showed no significant difference between them. As such, we report the Pearson correlation, as this test is more sensitive for the identification of outliers. Both test were performed using Rstudio (version 3.1.0).

2.4. Results

2.4.1. Characterising metal pollution in the catchment

In water samples, metal concentrations occurred in the following order for total: Zn>Fe>Sr>Ba>Pb>Al>Mn>Cd>Cu and dissolved forms: Zn>Fe>Sr>Ba>Al>Pb>Mn>Cd>Cu (Appendix 2.1). Two metals, Zn and Pb were chosen as the focus for this study based on their significant concentrations

derived from mining activities (Table 2.2). Annual pH averages reflected the considerable contribution of the underlying limestone bedrock showing a dominant circumneutral pH (mean= 6.8) in 80% of the studied sites. Some sites (e.g. H4 and H13) represent moorland runoff with little interaction with underlying rock, thus pH is lower (<6.3) due to high DOC and no carbonate buffering.

Table 2. 2. Mean, maxima and minima from water chemical analysis. Metal forms are denoted as total (T) and dissolved (D). Description of sites are indicated as main channel (MC), ephemeral tributaries (ET) and perennial tributaries (PT). Units are in μg/l. Values below the detection limit are represented by (b/d).

Site	Description		Pb_T	Pb_D	Zn_T	Zn_D
H15	Reservoir	Ave	316.7	279.6	2058.8	2028.0
		Max	411.9	423.6	2542.4	2759.5
		Min	96.3	103.6	722.4	1080.7
H14	PT	Ave	178.3	157.6	1318.6	1397.9
		Max	292.3	375.5	1778.9	2193.1
		Min	106.9	75.7	864.7	900.3
H13	ET	Ave	227.1	205.9	260.4	207.4
		Max	331.3	283.4	1619.8	1435.5
		Min	141.2	138.0	b/d	b/d
H12	ET	Ave	686.4	284.2	5168.8	4252.3
		Max	2701.2	439.9	12619.3	7438.4
		Min	261.8	184.1	66.5	73.6
H11	PT	Ave	64.0	31.6	295.7	410.5
		Max	765.6	355.2	3493.9	5276.2
		Min	3.7	b/d	b/d	b/d
H10	MC	Ave	108.1	80.7	468.8	444.4
		Max	268.1	145.2	787.4	777.0
		Min	11.8	3.1	b/d	b/d 33.5
H9	PT	Ave	28.5	20.8	125.2	95.7
		Max	171.9	94.3	572.2	518.6
		Min	12.7	2.0	b/d	b/d
H8	ET	Ave	38.1	19.0	318.5	269.0
		Max	123.5	28.2	438.3	435.2
		Min	12.2	5.3	b/d	b/d
H7	PT	Ave	7.7	4.3	3440.2	3220.5
		Max	21.1	47.7	5425.8	4312.3
		Min	0.8	b/d	2062.0	1936.7
H6	MC	Ave	60.4	49.4	537.6	510.2
		Max	102.0	85.6	664.1	674.1
		Min	20.5	13.8	468.3	390.2
H5	PT	Ave	60.4	54.3	883.5	867.2
		Max	132.3	157.8	1216.5	1206.0
		Min	17.1	10.0	688.0	613.5

Table 2.2 (continued). Mean, maxima and minima from water chemical analysis. Metal forms are denoted as total (T) and dissolved (D). Description of sites are indicated as main channel (MC), ephemeral tributaries (ET) and perennial tributaries (PT). Units are in μg/l. Values below the detection limit are represented by (b/d).

Site	Description		Pb_T	Pb_D	Zn_T	Zn_D
H4	ET	Ave	8.3	4.4	b/d	b/d
		Max	26.7	6.6	68.6	68.6
		Min	3.2	b/d	b/d	b/d
H3	PT	Ave	2.8	0.2	b/d	b/d
		Max	10.6	0.7	98.6	84.7
		Min	0.05	b/d	b/d	b/d
H2	MC	Ave	46.7	39.4	515.0	485.9
		Max	93.5	87.4	765.4	606.9
		Min	17.0	4.2	194.5	360.5
H1P	PT	Ave	3.0	1.9	b/d	b/d
		Max	5.2	8.3	68.6	68.5
		Min	0.8	b/d	b/d	b/d
H1	MC	Ave	31.1	16.6	217.5	158.9
		Max	146.8	43.7	375.9	302.9
		Min	5.1	b/d	77.9	67.8

Across the catchment, Zn_D was the most abundant pollutant with concentrations ranging from 95.7 to 3220.5 μg/l in perennial tributaries. Ephemeral tributaries also showed high concentrations up to 4252.3 μg/l while sites along the main channel had Zn_D concentrations from 158.9 to 510.2 μg/l. The second toxic pollutant of concern was Pb_D, where main contributions were observed in ephemeral tributaries with ranges from 4.4 to 284.2 μg/l, and perennial tributaries ranged from 1.9 to 157.6 μg/l. The main river channel showed concentrations of Pb from 16.6 to 80.7 μg/l. Major cations were dominated by calcium, with concentrations from 2.6-54.9 mg/l, and major anions comprised sulphate (3-24.9 mg/l), nitrate (1-17.8 mg/l), phosphate (0.002 to 0.1 mg/l) and chloride (7.2-10.5 mg/l). Dissolved inorganic carbon concentrations ranged from 0.9 to 42.7 mg/l and dissolved organic carbon from 1.2 to 16.8 mg/l (Appendix 2.2). Field blank measurements showed concentrations below limit for all the elements and

replicates with a standard deviation of ≤ ±0.5 μg/l (Cd and Cu), ≤ ±3.6 μg/l (Mn and Sr), ≤ ±12 μg/l (Pb, Al, Ba).

From mineralogical analysis of spoil and sediment samples, the most abundant minerals were quartz (SiO_2) and fluorite (CaF_2). Spoil samples (B1, B2 and GM) included barite ($BaSO_4$) as an additional dominant mineral. Other secondary minerals like muscovite ($KAl_2(Si_3AlO_{10})(OH)_2$) and kaolinite ($Al_2Si_2O_5(OH)_4$) were present at B1 and GM. Furthermore, the mineral cerussite ($PbCO_3$) was detected at B1. In sediments (H14, H12, H10, H1), the mineralogy of H14 was similar to B2 (principally the presence of quartz, fluorite and barite) whereas H12 and H10 contained calcite ($CaCO_3$), and H1 (140 m from the confluence with the River Wharfe) presented mainly quartz and calcite. Chemical composition analysis detected significant fractions of Pb in spoils B1 (35.1 g/kg) and Zn in GM (34.2 g/kg), while for sediments, major Pb concentrations were present in H12 (15.3 g/kg) and Zn in H14 (11.9 g/kg). Total Pb plus Zn in the sediment samples showed a decrease the further downstream the sample origin (Figure 2.2). Analysis of water composition and surface area in spoil samples showed higher percentages of water composition in GM (34.29%) followed by B2 (18.77%) and B1 (18.6%), while surface area values were: GM (20.6 m^2/g), B1 (5.82 m^2/g), B2 (1.34 m^2/g).

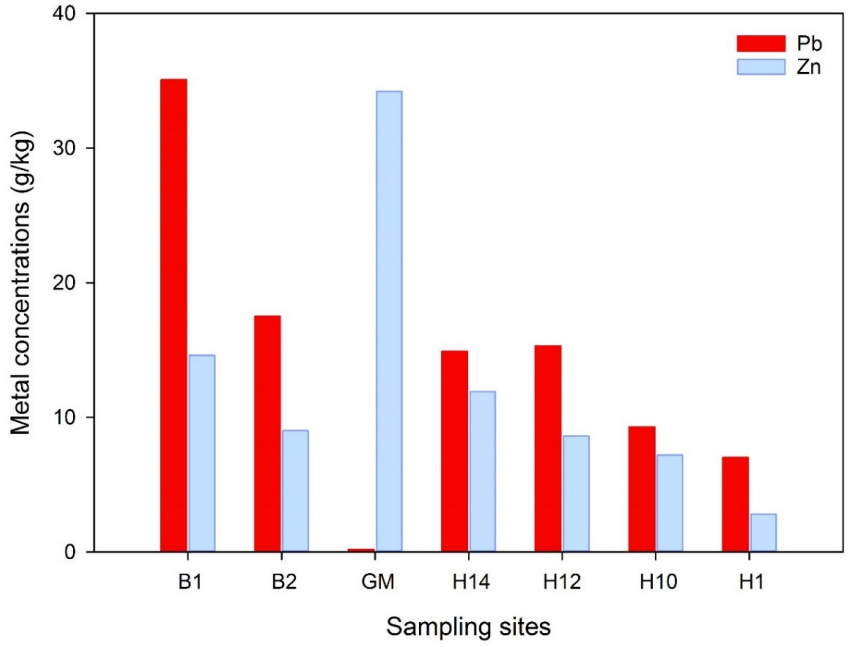

Figure 2. 2. Lead and zinc composition in spoils and sediments.

2.4.2. Mineral phases controlling dissolved metal concentrations

The metals Zn and Pb are the most significant toxic pollutants derived from mining activities. However, we modelled the geochemical behaviour of the additional metals Al, Fe, Ba and Sr as they are present in significant concentrations in the catchment. Geochemical modelling predicted that kaolinite ($Al_2Si_2O_5(OH)_4$) may account for the Al source with the solubility being controlled mainly by amorphous Al oxide phases ($Al(OH)_3$). Concentrations of Fe are more likely derived from secondary minerals. Iron solubility is controlled by amorphous phases such as ferrihydrite ($Fe(OH)_3$). The supersaturation of the Al and Fe phases may suggest the presence of some colloidal metal measured as part of the dissolved fraction. Barium concentrations are controlled by barite ($BaSO_4$), while Sr activity was too low to infer a controlling phase, perhaps being controlled by a mineral where it is present as a secondary metal. Lead and Zn concentrations are largely regulated by secondary minerals as metal-carbonates, cerussite ($PbCO_3$) and smithsonite ($ZnCO_3$), respectively (Figure 2.3).

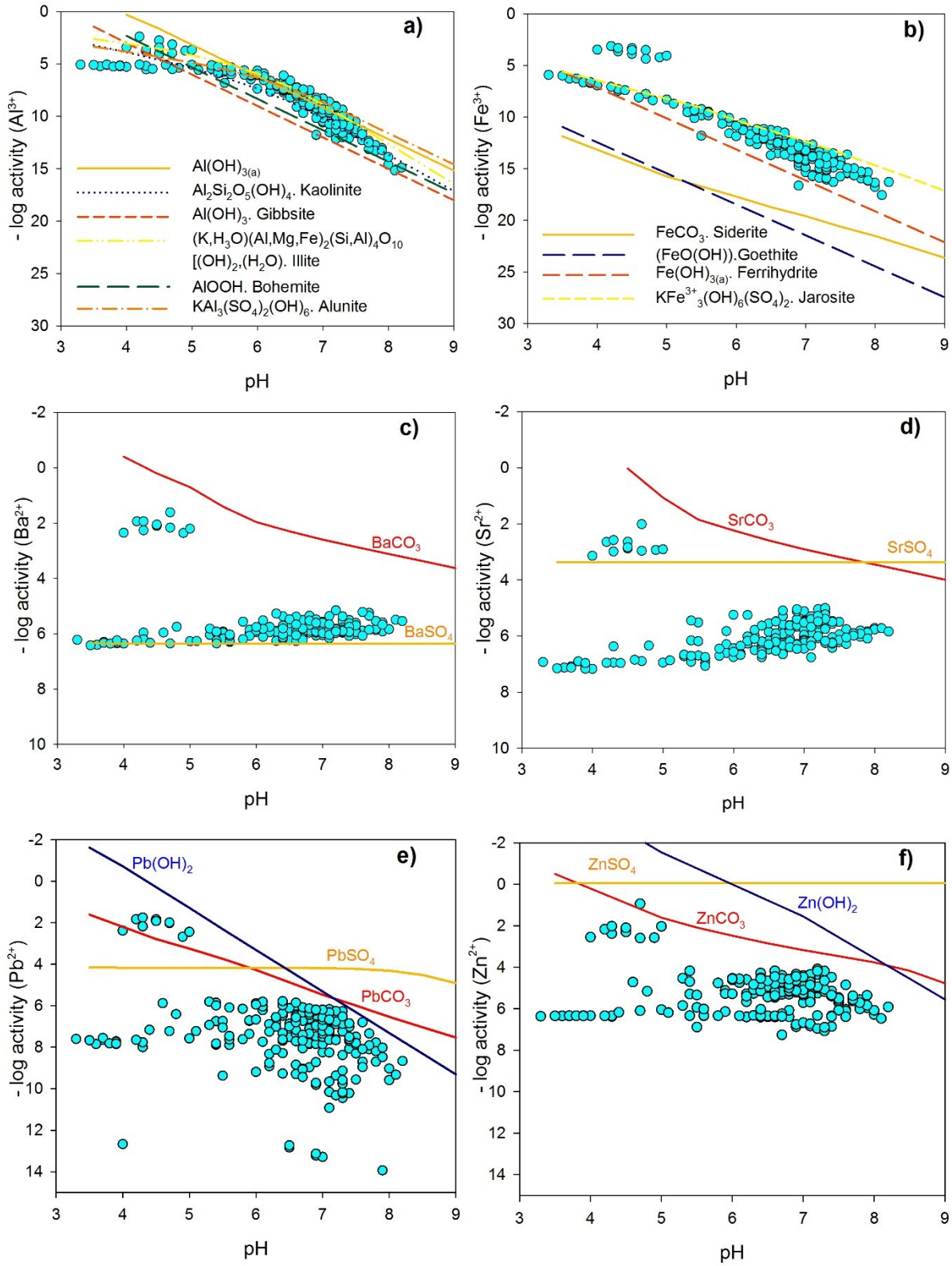

Figure 2. 3. Aluminium, Fe, Ba, Sr, Pb and Zn activity as a function of pH, SO_4^{2-} (13592 μg/l), Cl^- (7730 μg/l) and pCO_2 = 0.0012 atm. Theoretical saturation of mineral forms are represented by solid lines and calculated metal free ion activity of experimental data by dots.

2.4.3. Key chemical relationships

Table 2.3 summarises correlation analysis of metals derived from mining activities (Pb, Zn) and bedrock weathering (Ca) with major water chemistry parameters (pH, SO_4^{2-}, DIC and DOC) (Appendix 2.3). Zinc presented good correlation with SO_4^{2-} (r= 0.6), Ca showed very strong association with DIC (r= 0.9), while Pb presented poor correlations (r≤ 0.3). Principal component analysis (PCA) shows key geochemical processes in influencing the water chemistry of Hebden Beck (Figure 2.4). The first component (PC1) with a 32% of variance indicates strong correlations between dissolved and particulate forms of calcium, magnesium, with DIC, EC and pH, reflecting weathering of the bedrock, while moderate correlation between iron and DOC refers to the transport of metals through colloidal matter in aquatic systems. Furthermore, the second component (PC2) with 21% of variance shows good correlations between strontium, zinc and cadmium with SO_4^{2-}, reflecting the oxidation of sulphide minerals. Other *in situ* parameters like temperature, DO, flow and anions (NO_3^- and Cl^-) were not significantly associated with metals when considering all sites.

Table 2. 3. Relationships between metals (Pb, Zn, and Ca) with pH, $SO4^{2-}$, DIC and DOC. Pearson correlation coefficient is denoted as r, p-value as p and confidence interval (95%) as CI.

Metals	Stats	pH	$SO4^{2-}$	DIC	DOC
Pb_D	r	-0.1	-0.1	-0.4	0.3
	p	0.084	0.194	<0.001	<0.001
	CI	[-0.257 0.016]	[-0.228 0.047]	[-0.517 -0.284]	[0.135 0.393]
Zn_D	r	0.2	0.6	0.04	-0.2
	p	0.008	<0.001	0.588	0.022
	CI	[0.051 0.319]	[0.517 0.692]	[-0.101 0.176]	[-0.295 -0.024]
Ca_D	r	0.6	0.7	0.9	-0.6
	p	<0.001	<0.001	<0.001	<0.001
	CI	[0.526 0.698]	[0.571 0.730]	[0.963 0.978]	[-0.701 -0.529]

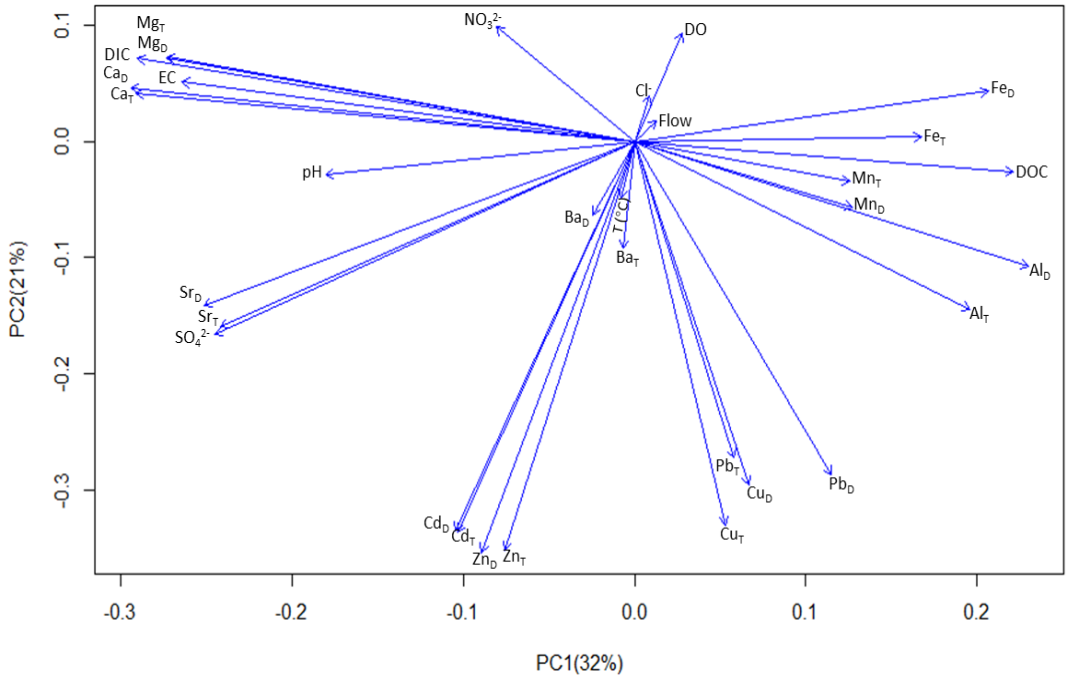

Figure 2. 4. Scree plot from PCA analysis, horizontal axis shows projections of the first principal component PC1 which represents 32% of the total variance and the vertical axis the second component PC2 representing the 21% of variance.

Complementary linear regression analysis was carried out at sites with highest concentrations of Zn_D and Pb_D (H15, H14, H12 and H7) for evaluating their relationships with DIC and SO_4^{2-}. Since H15 is a reservoir with lower variance in chemical concentrations, it was not considered for this and subsequent analyses. Strong correlations between Zn_D and DIC (R^2= 0.95) and SO_4^{2-} (R^2= 0.93) were identified at H7. Moderate correlations between Zn_D and SO_4^{2-} (R^2= 0.4) and between Pb and DIC (R^2= 0.5) were present at site H12 (Figure 2.5 and 2.6). No significant correlation was evident at site H14, therefore results are not shown.

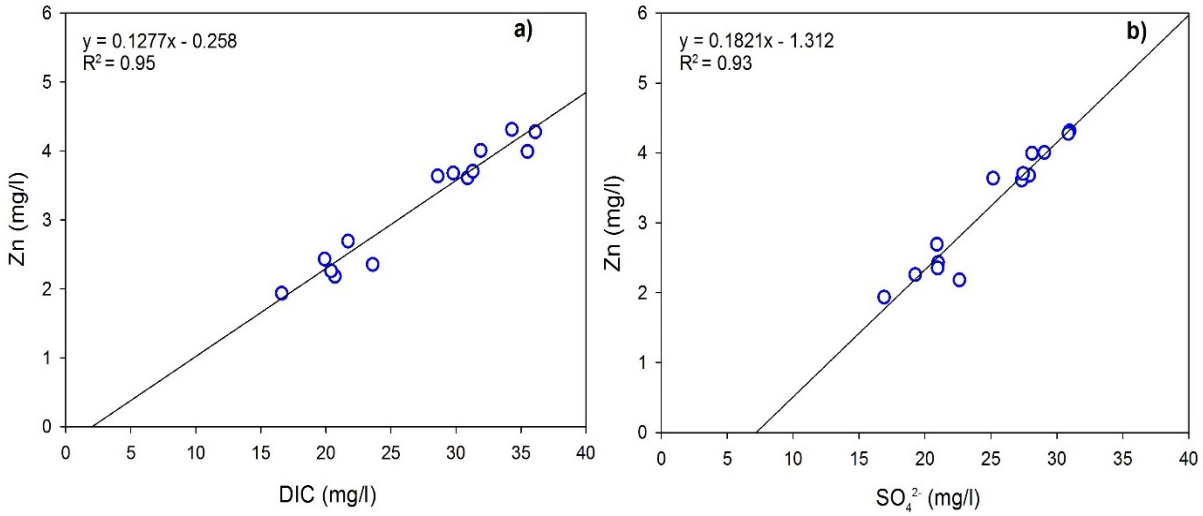

Figure 2. 5. Relationships in tributary H7 between Zn_D and DIC (left panel) and SO_4^{2-} (right panel).

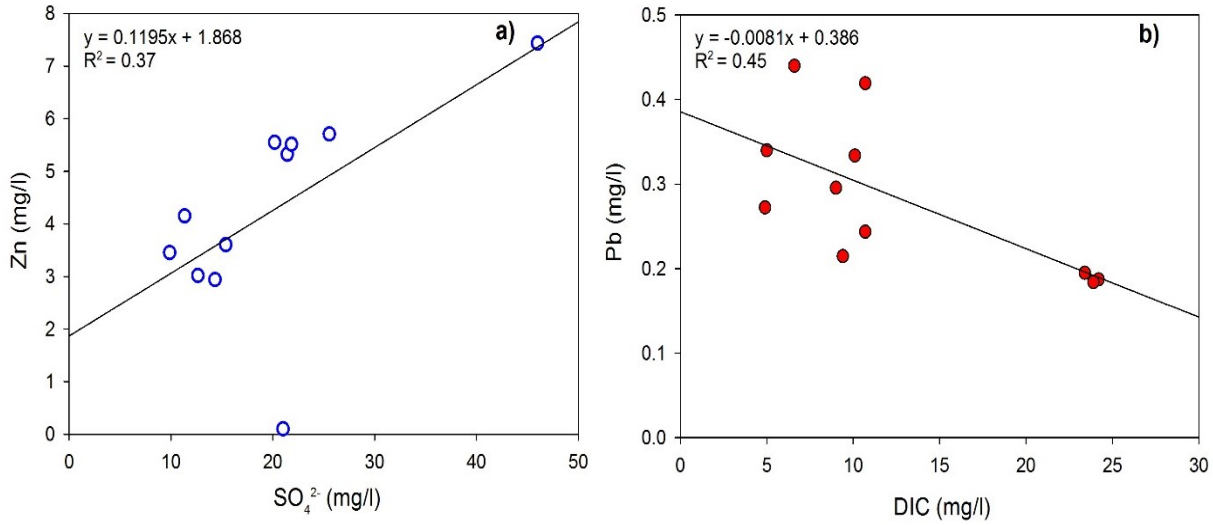

Figure 2. 6. Relationships in tributary H12 between Zn_D with SO_4^{2-} and Pb_D with DIC.

2.4.4. Seasonality and trends

Across the sampling campaigns, water temperature ranged from 3.6 to 15.6 °C, with higher values in summer (July) and lowest in winter (February). Consistent with temperature, low monthly average of EC values were recorded in winter (78 μS/cm) and high average values during summer (209 μS/cm). Dissolved oxygen levels showed similar values, ranging from 10.2-14.0 mg/l, with lower concentrations recorded in winter (December) and highest levels in autumn (September). For flow, highest annual rates were recorded in November (2666.1 l/s) and lowest rates in July (54.0 l/s) (Appendix 2.4).

Fluctuations were also dependent on the type of tributaries (e.g. perennial and ephemeral) (Appendix 2.5). Flow values in perennial tributaries ranged from 3.0 to 192.7 l/s and in ephemeral from 9.0 to 57.0 l/s when flow was measurable, as some tributaries were dry for 5 or 6 months. Across all tributaries, two significant sites were identified as metal contributors of Zn_D (H12: 4252.3 μg/l and H7: 3220.5 μg/l) and Pb_D (H12: 284.2 μg/l) (Table 2.1). Across all sites, mean values of pH were highest in September (7.1) and lowest in November 2013 (5.6) (Appendix 2.4). In individual sites, pH means ranged from 3.9 to 7.5, showing large monthly variations (SD≥ ±0.7) in sites H15, H11, H9, and H1P. Despite these variances a circumneutral pH (6.2-7.4) was predominant in the catchment.

Trends of flow and pH were considered to analyse their influence on metals concentration. Regression analysis was performed using all sampling sites. However, the results demonstrate the site specific nature of trends, with no catchment wide trends were revealed (Appendix 2.6). We investigate further the trends for H2, as the chemistry is representative of a significant distance of the downstream reach and it has limited dilution before entering the River Wharfe. Strong positive relationships were present for Pb_D-flow (R^2= 0.51) and Zn_D-pH (R^2= 0.58) and no clear relationships for Pb_D-pH (R^2= 0.06) and Zn_D-flow (R^2= 0.02) (Figure 2.7).

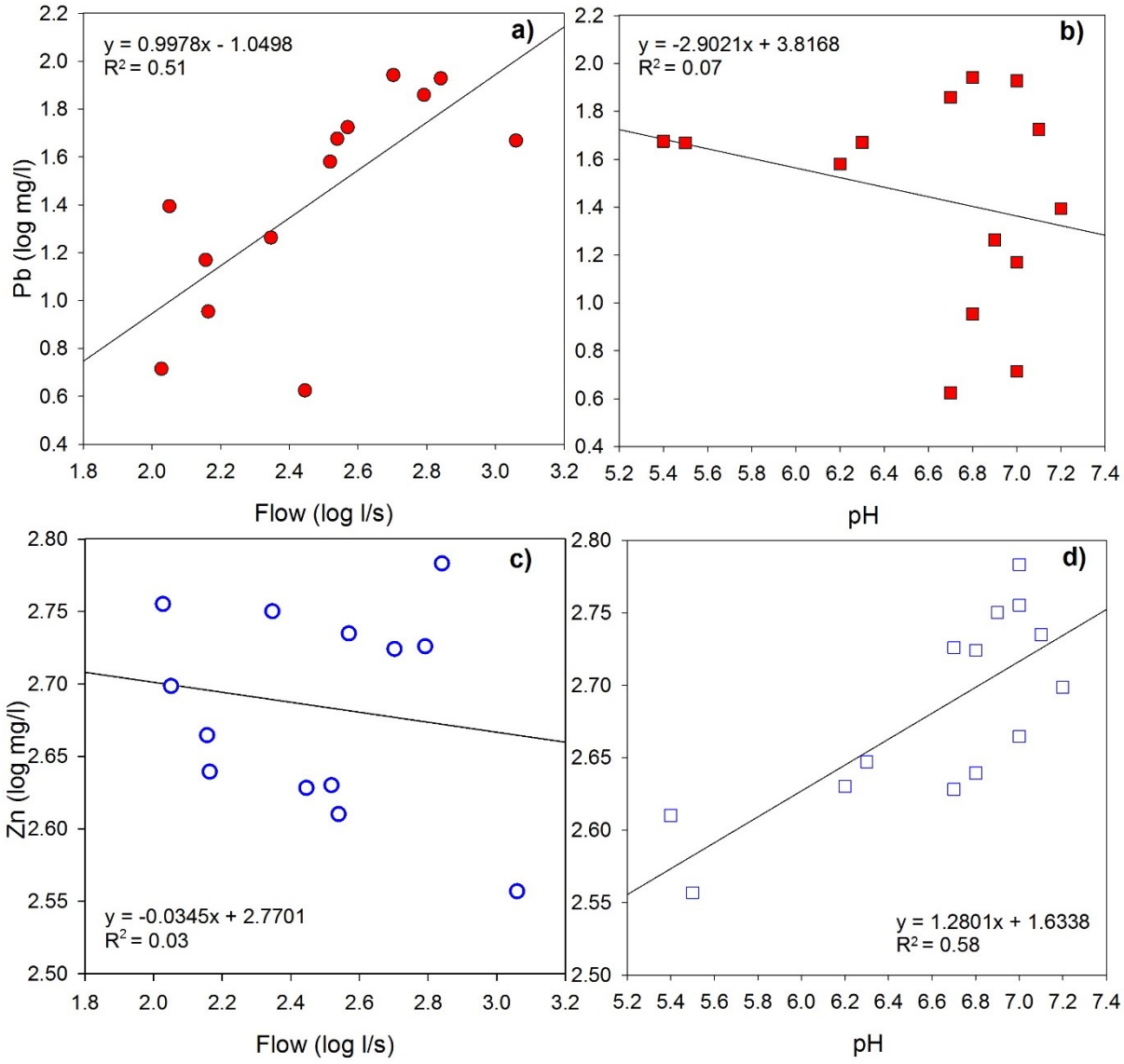

Figure 2. 7. Trends of metals in function of flow and pH in H2. Panel a and b show trends of Pb and panel c and d indicate Zn trends. Solid lines represent regression lines.

2.4.5. Annual metal load

The contribution of Pb_D and Zn_D in the catchment was estimated through the annual metal load (tonne/year). Only site H2 was considered for this calculation due to the availability of flow data and the lack of significant additional mine runoff downstream. Table 2.4 shows the average annual load of Pb is 0.2 tonne/year and for Zn 2.9 tonne/year. These values were compared with well-established EQS metals and showed maximum exceedances of 12-fold for Pb and Zn.

Table 2. 4. Estimation of annual Pb and Zn load by using flow records from Environment Agency (EA) gauging station at H2 (main channel).

Stats	H2-Flow (l/s) from EA station	Pb_D (µg/l)	Pb_D (tonne/year)	Zn_D (µg/l)	Zn_D (tonne/year)
Average	189	39.4	0.2	485.9	2.9
Maximum[(a)]	556	87.4	1.5	606.9	10.0
Minimum[(b)]	36	4.2	<0.1	360.5	<0.9
EQS-Hardness based		*7.2*		*50.0*	

a) Maximum values recorded in February 2014.
b) Minimum values recorded in July 2014.

2.5. Discussion

In the catchment, biogeochemical actions such as weathering and erosion are significant processes in the generation of dissolved metals, which are likely derived from bedrock weathering and oxidation or dissolution of mineral ores. Carboniferous limestone bedrock, mainly composed of calcite ($CaCO_3$) is weathered, releasing significant amounts of calcium and carbonate, and creating a neutralizing capacity and circumneutral pH in environments surrounded by sulphide ore wastes. The influence of the geology in the catchment was shown by strong relationships between Ca_D with DIC ($r= 0.9$, $p<0.001$) and pH ($r= 0.6$, $p<0.001$). For metals derived from mining activities, a potential primary source of Zn_D is the oxidation of sphalerite (ZnS) as a good correlation was observed between Zn_D and SO_4^{2-} ($r= 0.6$, $p<0.001$) (Table 2.3). However, additional Zn_D concentrations may be attributed to the presence of secondary zinc minerals (e.g. smithsonite) (Tame et al., 2017). Contributions of Pb_D are associated with dissolution of metal-carbonate compounds (cerussite) rather than oxidation of metal-sulphide as no correlation between Pb_D with SO_4^{2-} was identified ($r\leq -0.1$,

p<0.001) (Table 2.3). The presence of secondary minerals such as metal-carbonate might affect the solubility and mobility of metals as they present slower dissolution kinetics than primary minerals (Nuttall and Younger, 2002; Carroll et al., 1998; Carmona et al., 2009; Jamieson, 2011).

Geochemical modelling has revealed the importance of secondary minerals such as carbonates, sulphates and hydroxides in the control of dissolved metals (Figure 2.3). For instance, Pb and Zn concentrations are greatly influenced by the dissolution of metal-carbonate forms (e.g. cerussite and smithsonite) (Li and Thornton, 2001; Nuttall and Younger, 2002). Carbonates released from the dissolution of metal-carbonate also contribute to the river alkalinity, enhancing the buffering capacity of the system. In addition, the source of Al can be associated with the presence of kaolinite, which was identified by the XRD analysis in most of the spoils/sediments. The presence of Fe concentrations can be associated with jarosite, and although this mineral was not detected by XRD analysis, it is a common secondary Fe mineral in mining areas (Cravotta Iii, 2008b; Sánchez España et al., 2005). Figure 2.3 shows that Fe activity follows closely the prediction for jarosite, which at pH > 3 tends to dissolve and release sulphate ions and Fe^{3+} (Ettler et al., 2003). In alkaline environments the activity of Fe^{3+} is likely controlled by hydrous ferrous oxides, the presence of colloids in the dissolved fraction may explain the supersaturation. Aluminium and Fe solubility are controlled by amorphous phases, specifically $Al(OH)_3$ and $Fe(OH)_3$ (known as ferrihydrite). The presence of hydroxide compounds in the catchment could affect metal mobility, as they might sorb or co-precipitate with metals like Pb and Zn, acting as natural scavengers of these toxic elements (Balistrieri et al., 1999). Nordstrom (2011) indicated that hydrology is another factor influencing metal mobility as concentrations of constituents in natural waters depend to a large extent on the rate of dissolution relative to flow rate. This condition was observed in the upper site of the catchment (a pond) as concentrations of metals were closer to saturation due to longer residence time of the water than under stream flow conditions (Appendix 2.6). Clustered sites with high metal free ion activities were identified and associated with sites with low pH values (<5), possibly caused by high DOC concentrations (>8 mg/l), which are not considered

in the modelling. The presence of metal-organic complexes will reduce the activities of metal free ions.

Analysis of sediments and spoils were consistent with water chemistry results showing Zn (11.9 and 34.2 g/kg) and Pb (15.3 and 35.1 g/kg) as major metals present in spoils due to lower extraction efficiency methods common in historical mining (Gill, 1993). Preliminary sequential batch leaching experiments of spoil samples into deionised water showed consistent Zn and Pb concentrations of at least one order of magnitude above other metals across several leaching cycles (except Pb in GM where it is not present in significant concentrations). For leaching with acid (0.1 M HCl) most Zn was solubilised in the first two batches. Similar concentrations of Pb and Ca were leached but over five acid addition cycles, suggesting different dissociation kinetics of Pb and Zn minerals (Osbourn and Stockdale, 2016). Future work will further explore the kinetics of leaching from the mineral forms in the spoils and sediments. Mineralogical results revealed the presence of secondary minerals such as cerussite ($PbCO_3$) as a source of Pb. Current chemical characterisation is in agreement with previous studies of water quality, metal composition and flux in the Yorkshire Pennine Orefield (Jones et al., 2013).

The impact of former metal mining on water quality has been evidenced by Pb, Zn and Cd pollution in the Yorkshire Pennine region, particularly in Hebden Beck (Jones et al., 2013; Barber, 2014). In expanding the range of Hebden Beck tributaries from earlier works, we have included sites close to mine wastes (e.g. tailings, spoils) for the identification of principal sources of metals. Major contributions of Zn_D and Pb_D were identified from mine water discharges (H7) and spoil wastes (H12) (Jones et al., 2013). For these two sites there are statistically significant relationships between Zn and Pb with SO_4^{2-} and DIC inferring the composition of their respective mineral sources. At site H12, an extended area covered by spoil wastes from Yarnbury mines, moderate correlations were identified between Zn_D with SO_4^{2-} (R^2= 0.37), and Pb_D with DIC (R^2= 0.45) reflecting the Zn_D contribution from the oxidation of sphalerite and Pb_D contribution from the dissolution of cerussite (Figure 2.6). These correlations

revealed the type and grade of ores mined during the eighteen and nineteenth centuries, producing spoils with different particle sizes and permeabilities, influencing their capacity to form secondary minerals (Palumbo-Roe et al., 2013). At site H7, a mine channel from Bolton Haw, strong correlations were observed between Zn and SO_4^{2-} (R^2= 0.93) and Zn and DIC (R^2= 0.95) (Figure 2.5). Both correlations suggest the oxidation of sphalerite as the main Zn source, however, if all sulphate was from ZnS the expected molar ratio between Zn_D and SO_4^{2-} should be 1:1 instead of the observed value of 5:1. Furthermore, the mineralogical and geochemical results did not show extensive evidence of pyrite mixed in mineral veins (correlation of Fe/SO_4^{2-} r= -0.5; p= 0.076). Likewise, Dunham and Wilson (1985) have reported that although pyrite, marcasite (FeS_2) and bravoite ((Fe, Ni, Co)S_2) are abundant in the orefield, they are found in minor amounts in veins, representing small quantities in relation with adjacent deposits rich in Fe discharges. Thus, secondary zinc minerals such as smithsonite ($ZnCO_3$), hydrozincite ($5ZnO.2CO_2.3H_2O$) and hermimorphite ($Zn_4[Si_2O_7](OH)_2.H_2O$), should be considered as possible sinks (Nuttall and Younger, 2002). No correlation for Pb was observed in this site, probably due to the presence of low concentrations (4.3 μg/l) as a consequence of aging (Iavazzo et al., 2012) or the sorption effect of biofilms, becoming a significant sink for Pb (Templeton et al., 2001).

In Hebden Beck, flow events can alter the river water chemistry and metal concentrations (Jones et al., 2013). During base flow conditions, the circumneutal pH and buffering capacity are maintained by groundwater rather than surface water. This condition contributes to the presence of secondary zinc minerals and other carbonate minerals that sequester zinc, also influences the complexation of Pb with carbonate and organic matter, and affects its transformation to other forms like hydroxide, oxyhydroxide, hydroxysulfate minerals, limiting solubility and further weathering (Nuttall and Younger, 2002; Nordstrom, 1982; Nordstrom, 2011; Jamieson, 2011). Flow fluctuations caused by drought or heavy rainfall allowed the identification of major point and diffuse sources (H7 and H12) and their metal contributions under different flow events. At the point source H7 (mine adit-Bolton Haw), metal concentrations were generally constant at both flow

conditions, therefore this site can be considered as a continuous source of metals (particularly for Zn: 3220.5 μg/l). At the diffuse source H12 (ephemeral tributary-draining spoil wastes from Yarnbury mine), metal concentrations become more significant during high flow, but greater contributions were also observed after dry periods (e.g. July [0 l/s, Zn_D and Pb_D below detection limits], August [8.4 l/s, 5709.0 μg Zn_D/l, 419.2 μg Pb_D/l]). This might be explained by the capacity of soluble sulphate minerals to store metals (e.g. Zn) during dry seasons and release them into the environment during wet seasons (Jamieson et al., 2005). In addition, Byrne et al. (2009) and Cánovas et al. (2008) have indicated the influence of runoff produced by storms in increasing metals dissolved from weathered metal salts (smithsonite, cerussite) located in superficial mine spoils. Rothwell et al. (2007) showed differences in metal concentrations not only between base and high flow conditions but also within and between storm events. Thus, further studies of metal concentrations and fluxes under a range of hydrological conditions are pertinent since the frequency and magnitude of floods are increasing the transport of dissolved and particulate metal forms from sources to river channels and floodplain soils, which are often used for agriculture (Lynch et al., 2014).

Seasonal variations of pH and flow were considered to assess metal mobility. In the main channel (H2) strong correspondence occurred between pH-Zn_D (r= 0.7) and flow- Pb_D (r= 0.6) while relationships for Pb_D-pH and Zn_D-flow were unclear. The absence of a relationship of Zn with flow suggests that dissolution of zinc minerals is not kinetically limited (Figure 2.7), although solubility has been shown to depend on mineral composition in some cases (Palumbo-Roe et al., 2013). The Pb relationship with flow may be related to greater flushing of areas where minerals have had longer to leach Pb into waters (e.g. H15 or the ephemeral pond feeding H12) (Appendix 2.7). Sims et al. (2013) have also reported the role of flow in the generation of suspended matter, affecting the transport Pb forms. Once they enter into the aquatic system they tend to be adsorbed to suspended matter, while for the case of carbonate minerals they are likely to break down in acid waters, liberating significant quantities of Pb to sediments further down the

river (Hudson-Edwards et al., 1996). Thus, understanding the chemical tendencies of Zn and Pb under local pH and flow conditions is extremely important for estimating the potential fate and extent of polluters.

Metal contributions from point and diffuse sources decreased downstream (H2) (Zn_D: 479.4 μg/l, Pb_D: 35.1 μg/l), indicating a dilution effect from non-mine affected tributaries. Two dilution behaviours were observed in the main river, an abrupt reduction of Zn_D after high concentrations were converged with relatively clean tributaries (from 3220.5μg/l (H7) and 4252.3μg/l (H12) to 444.4μg/l (H10)), and a gradual decrease of Pb_D (284.2μg/l (H12) to 80.7μg/l (H10)) as dilution is likely to be related to the distribution of particulate matter from sediments (Douben, 1989). Pb forms showed a higher fraction present as particulate (≥50%) in certain tributaries (e.g. H12, H11, H8, H3, H1) where dissolved organic carbon (H12 and H11>16 mg/l) and other complexing compounds like bicarbonates (DIC in H8, H3 and H1>22 mg/l) or hydroxides (e.g. $Fe(OH)_3$ and $Al(OH)_3$) may bind Pb. Thus, knowing solubility and speciation properties of Zn and Pb could help in the explanation of their mobility. Low solubility of Pb conceals high concentrations released at diffuse sources, due to binding to particulates (Langmuir, 1997). In addition, sorption properties also affect metal dynamics, for instance, Pb has a greater affinity for binding to dissolved organic matter and surface reactive mineral complexes, as reflected in higher fractions present as particulate forms. These mechanisms are fundamentally associated with metal speciation, bioavailability and toxicity. The bioavailability of Zn and Pb in Hebden Beck has been assessed, revealing quality standard failures of Pb and Zn throughout the catchment at all monitoring sites (Barber, 2014).

Calculations of the dissolved Zn and Pb being transported downstream to the River Wharfe indicate annual loads of 0.2 tonnes/year of Pb and 2.9 tonnes/year of Zn. Although, these loads might increase depending on physical or chemical conditions caused by seasonal variations or particular flow conditions. Several studies in river systems have reported that metals associated with suspended sediments can make a major contribution to the total load of metals (Foster and Charlesworth, 1996; Horowitz et al., 1995). Horowitz (1991) compared and

contrasted metal concentrations in suspended and bottom sediments versus dissolved levels, results indicated that bottom sediment concentrations were more than 100,000 (5 orders of magnitude) times higher than dissolved levels. Applying this approach in a downstream site (H1), higher results were observed for Pb (>430,000) and to a lesser extent for Zn (>17,000). Considering the importance of sediments in the transport and cycling of metals further work is needed in Hebden Beck. Comparisons between maximum measured concentrations of total dissolved metal concentrations in the main channel (site H2) with established regulatory limits for metals indicated that maximum annual concentrations of Al_D (188 μg/l), Fe_D (657 μg/l), Ba_D (306 μg/l) and Sr_D (356.4 μg/l) were within established regulatory limits (e.g. Al: 200 μg/l; Fe: 1000 μg/l; Ba: 1000 μg/l; Sr: 1500 μg/l). Conversely, maximum annual concentrations of Pb_D (87 μg/l) and Zn_D (607 μg/l), when compared with environmental quality standards (EQS) showed maximum exceedances of 1200% with likely ecological effects (UK-Environment Agency, 2011; Department of Environmental Protection and State of New Jersey, 2017) (Table 2.4).

Metal toxicity and bioavailability are mainly controlled by metal concentrations, pH conditions and concentration of organic matter. Although the last two factors might have a stronger effect on biotic communities. For example, Ramsey (2006) reported that soil acidity and organic matter concentration exerted stronger effects on plant and microbial community than metals. Thus, discriminating the influence of these key factors in biological processes is important from the perspective of dealing ecotoxicological effects of metals and potential restoration efforts (Miller et al., 2004; Dennis et al., 2009). In this context, environmentally friendly and cost-effective techniques such as bioremediation have been developed for heavy metal removal/recovery where microbial remediation is particularly used in mine drainages due to the ability of microorganisms to generate alkalinity and immobilise metals (Mulligan et al., 2001). For instance, in the UK the sulphur-reducing bacteria (e.g. *Desulfovibrio vulgaris*) has been used in the treatment of mine drainage due to its diverse metabolic strategies to reduce sulphate (SO_4^{2-}) to hydrogen sulphide (H_2S), other elements like iron (Fe(III)),

oxygen and compounds like nitrate and nitrite and fumarate (Jarvis et al., 2015). Aquatic organisms such as diatoms and invertebrates have an important role as biomonitors and bioindicators for assessing the impact of metal pollution. These organisms together with established EU-WFD classification tools and diversity indices (e.g. ASPT, N-TAXA) were used in a preliminary assessment of this catchment, however the effects of elevated metal levels were unclear (Environment Agency, 2014). Studies in neutral mine drainage carried out by Byrne et al. (2013) indicated that the use of standard macroinvertebrate biotic and diversity indices (EU-WFD tools) could lead to erroneous classifications of aquatic ecosystem health. These results revealed that failure in the interpretation of biogeochemical interactions could lead to inaccurate analysis of organisms at risk of exposure, hence ineffective management decisions. Thus, the assessment of metal effects on living organisms is complex since biota might have different responses according to physiological processes, and because metals are subject to a range of factors affecting their level of reactivity, toxicity and bioavailability (Luoma, 2008). Considering WFD goals, more nuanced approaches are needed for assessing metals and their ecological effects. In this context, current chemistry data and updated chemical speciation tools will be used in future work to assess metal availability and toxicity and advising improvements to river basin management plans.

2.6. Conclusions

- Underlying limestone bedrock controls pH and weathering reactions, and therefore metal mobility within such catchments.
- Mobilisation of Zn and Pb have a strong dependence on site specific biogeochemistry and hydrological conditions. No dependence of Zn with flow suggests that Zn_D has no kinetic limitations on Zn mineral dissolution, whereas Pb_D varied according with flow variations, reflecting its tendency to be complexed with colloidal or particulate forms.

- Point sources are regular contributors of Zn_D despite flow fluctuations, while diffuse sources like spoil wastes produced higher contribution of Zn_D and Pb_D in overflow conditions after dry periods.
- Not all contributions of Zn_D and Pb_D are derived directly from oxidation of sphalerite and galena. Mineralogical and geochemical analysis revealed the contribution of secondary minerals such as smithsonite and cerussite, which are continuously leaching into the river and represent an added complexity for future remediation.
- Metal pollution results in a large area of catchment having a depleted chemical status with likely effects on the aquatic ecology.

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Chapter 3: Evaluating water quality and ecotoxicology assessment techniques using data from a lead and zinc effected upland limestone catchment

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Abstract

Point and diffuse sources associated with historical metal ore mining are major causes of metal pollution. The understanding of metal behaviour and fate has been improved by the integration of water chemistry, metal availability and toxicity. Efforts have been devoted to the development of efficient methods of assessing and managing the risk posed by metals to aquatic life and meeting national water quality standards. This study, focuses on the evaluation of current water quality and ecotoxicology techniques for the metal assessment of an upland limestone catchment located within a historical metal (lead ore) mining area in northern England. Within this catchment, metal toxicity occurs at circumneutral pH (6.2-7.5). Environmental Quality Standards (EQSs) based on a simple single concentration approach like hardness based EQS (EQS-H) are more overprotective, from sixteen sites monitored in this study more than twelve sites (>75%) failed the EQSs for Zn and Pb. By increasing the complexity of assessment tools (e.g. bioavailability-based (EQS-B) and WHAM-F_{TOX}), less conservative limits were provided, decreasing the number of sites with predicted ecological risk to seven (44%). Thus, this research supports the use of bioavailability-based approaches and their applicability for future metal risk assessments.

3.1. Introduction

Humans have impacted upland catchments for centuries through the process of mining. Exposure of metal-bearing minerals to oxygen and water, both subsurface and through dumping of mine wastes above the surface, can result in increased dissolved concentrations of metals in water bodies. Once metals have entered aquatic ecosystems, they interact with a broad spectrum of biotic and abiotic components via dynamic interrelated processes, resulting in a large variety of compounds (Luoma, 2008).

In natural waters, the behaviour of metals depends on their speciation. Such species include free ions, inorganic complexes, organic complexes, and metal sorbed to or incorporated within colloids or particulate matter. The formation of metal complexes depends on the concentration of all dissolved components, pH, and ionic strength (Namieśnik and Rabajczyk, 2010). Free metal ions can bind to dissolved organic matter (DOM; particularly humic acids), forming complexes that regulate the concentrations of metals available for interaction with organisms (Tipping, 2002). The complexity of these interactions in aquatic environments makes it difficult to measure the distribution of chemical forms. Knowledge of chemical speciation is important because the relative distribution of different forms controls metal interactions with organisms, including toxic effects. For instance, dissolved metals, particularly free metal ions, have been related to freshwater ecotoxicity (Campbell, 1995; De Schamphelaere and Janssen, 2002). More recently, the concentration predicted to be bound to humic acid has been found to be a good proxy for organism body burdens (Stockdale et al., 2010; He and Van Gestel, 2015).

In the last few decades, a variety of *in situ* analytical approaches have been developed to understand the dynamics of metals in natural waters (Buffle, 2000). One such technique is the Diffusive Gradients in Thin-films (DGT) for assessing a range of active species, depending upon their mobility (diffusion coefficients) and kinetics (dissociation rates) across a thin film of polyacrylamide gel (Zhang and Davison, 2015). This technique has been used as a monitoring tool for providing kinetic information on labile metal species in rivers, soil or sediment impacted by mines and coastal waters (Unsworth et al., 2006; Warnken et al.,

2009). In addition, DGT has been applied to investigate potential metal availability in freshwater ecosystems, for instance the accumulation of cadmium in communities of algae (periphyton) has been evaluated by Bradac et al. (2009).

In view of the importance of DOM in complexing metals, comprehensive speciation models have been developed for predicting the distribution of chemical species accounting for complexation with inorganic and organic ligands as well as competition for organic binding sites between different metals, and between metals and protons. The Non-Ideal Competitive Adsorption (NICA) coupled with a Donnan electrostatic sub-model uses a continuous distribution approach to describe metal and proton bindings to organic matter (Benedetti et al., 1995; Kalis et al., 2006). A discrete site approach is used in the Humic Ion Binding Model VII (Tipping et al., 2011). This is coupled with an inorganic thermodynamic code, the Windermere Humic Aqueous Model (WHAM) (Tipping, 1994). The WHAM code has been successfully applied in a variety of research and regulatory areas related to water quality criteria for zinc and copper in the United States and Europe (Hamilton-Taylor et al., 2011; Balistrieri and Blank, 2008; 2014; Cheng et al., 2005). In addition, it has been used across Europe as part of the Critical Loads approach related to atmospheric deposition and soil pollution by cadmium, lead, mercury and copper (de Vries et al., 2007; Hall et al., 2006; Tipping et al., 2003). Over recent decades, WHAM/Model V was incorporated into the Biotic Ligand Model approach to improve prediction of metal toxicity to aquatic organisms and support the implementation of Environmental Quality Standards (EQS).

Metal bioavailability and toxicity have long been recognized to be a function of water chemistry (Paquin et al., 2002). Until recently environmental regulations considered only hardness-based conditions to derive EQS (Beane et al., 2016). However, latest research has increased understanding of the influence of physicochemical variables in metal speciation, and ecotoxicological studies have extended our knowledge of metal effects on biota. Consequently, bioavailability-based approaches such as the Biotic ligand models (BLMs) have been implemented within EQS for chemical and ecological assessment, to evaluate the overall quality of a given waterbody (Niyogi and Wood, 2004). In the UK, the BLMs have been simplified to create a user-friendly method known as metal

bioavailability assessment tool (M-BAT), which use pH, DOC and calcium as input data to account for toxicity of single metals in freshwaters within a regulatory context (e.g. Zn-BLM, Cu-BLM, Mn-BLM and Ni-BLM) (De Schamphelaere and Janssen, 2002; Steenbergen et al., 2005; Lock et al., 2007). The M-BAT tools parameterised to date include those for Zn, Cu, Mn, Ni and Pb. Some of these tools have been incorporated into a tiered-approach monitoring scheme to implement the bioavailability-based water quality guidelines. However, they have limitations for assessing metal mixtures effects since they are based on BLMs for specific metal-organism, and they do not include all dissolved chemical species. To overcome this issue, an alternative bioavailability-based model (WHAM-F_{TOX}) developed by Stockdale et al. (2010) offers a plausible option for quantifying mixture toxicity and its potential effects on aquatic organisms. WHAM-F_{TOX} in common with the BLM uses organisms as reactants. However, WHAM-F_{TOX} assumes that toxicity is related to non-specific binding to organism surfaces rather than specific biotic ligands (Stockdale et al., 2010). Several studies have applied WHAM-F_{TOX} for predicting metal toxicity to aquatic biota in laboratory experiments and linking the effects of chemical speciation of metals and protons to species richness of freshwater macroinvertebrates (e.g. Ephemeroptera, Plecoptera and Trichoptera (SR_{EPT})) and zooplankton species diversity (Tipping and Lofts, 2013; 2015; Stockdale et al., 2010; 2014; Qiu et al., 2015).

Despite the scientific and regulatory improvements for the establishment of EQSs, achieving good ecological and chemical status of water bodies according to the Water Framework Directive (WFD) (European Commission, 2000) is still a significant challenge (UK-Environment Agency, 2008a). In the UK, the major impediment to meet this aim is related to diffuse pollution, including metal contamination generated by abandoned mines and mined wastes (Jarvis and Younger, 2000). At national scale, comprehensive data exist for certain areas but there are substantial gaps for other regions, therefore the assessment of the extent and severity of metal pollution from mining activities is partial (Mayes et al., 2009). As a consequence, the prioritisation of threatened sites to address remediation of metal pollution in a logical and cost-effective manner is a difficult task. River basin management plans (RBMP) provide a good framework for the

implementation of mitigation measures. But the application of bioavailability-based standards (EQS-B) offers a great support in the selection of sites at real ecological risk, reducing the burden of remediation targets for efficiently achieving a better quality of water bodies (UK-Environment Agency, 2008b; Harmsen and Naidu, 2013).

This study aims to evaluate different approaches used to assess water quality. Focusing on an upland limestone catchment affected by historical mining, we compare hardness based EQS with approaches that consider more detailed water chemistry such as BLM based EQS and WHAM-F_{TOX}. Data from a single biological survey were used to give context to the results from the chemical approaches. Additionally, we evaluate the ability of the DGT technique to yield dynamic dissolved concentrations that could be applied to EQS as the WFD allows for water quality criteria to be set based upon dynamic methods incorporating chemical speciation. This contribution complements a companion paper (Valencia-Avellan et al., 2017), which provided an assessment of the geochemical and hydrological processes controlling the main sources of metal pollution.

3.2. Methods

3.2.1. Site description

The study area is located within the Yorkshire Dales National Park, northern England (Figure 3.1). Hebden Beck is a headwater catchment containing extensive historical lead and zinc mining operations, which flows through limestone bedrock surrounded by sheep pasture and peat-rich moorland (Jones et al., 2013). Evidence of mining and smelting exists along the length of the river system, from mine tailings and slag to mine adits and abandoned buildings. A detailed description of the study area is provided in (Valencia-Avellan et al., 2017).

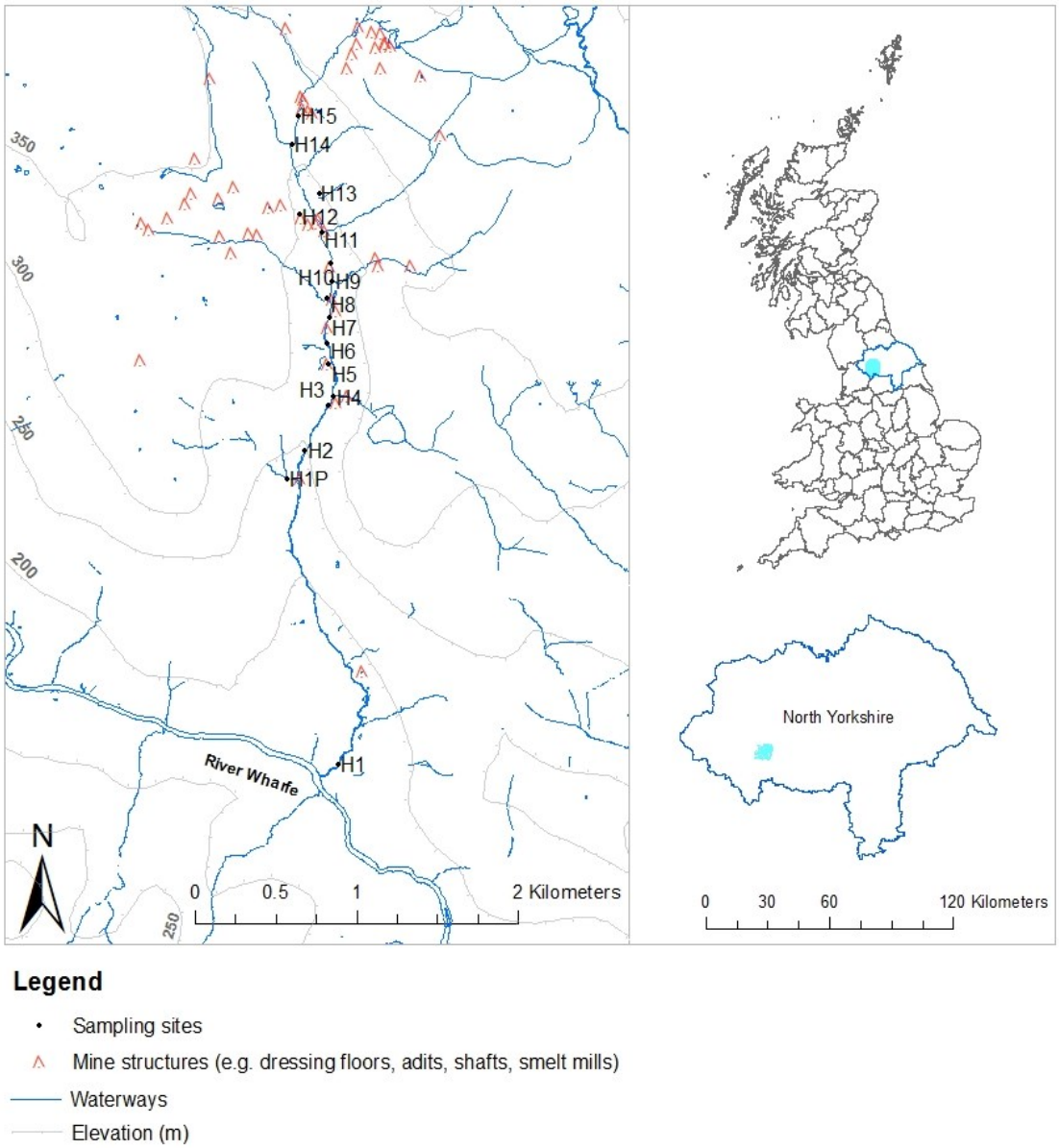

Figure 3. 1. Map showing location of Hebden Beck. Black dots represent sampling stations, they are ordered from upper to lower catchment, therefore from H15 to H1.

3.2.2. Water sampling

Monthly field surveys were conducted from November 2013 to December 2014 at sixteen sampling sites. Sampling locations (Figure 3.1) include a source pool, tributaries and the main river channel, covering an area of 5 km^2. The detailed sampling strategy and analytical procedures are described in Valencia-Avellan et al. (2017). Parameters recorded *in situ* such as temperature, pH, dissolved oxygen and conductivity, together with measured concentrations of dissolved metals (defined as filterable with a 0.45 μm filter) (Zn^{2+}, Pb^{2+} Cd^{2+}, and Cu^{2+}), major anions (SO_4^{2-}, Cl^-, NO_3^-, PO_4^{3-}) and dissolved carbons (DIC, DOC) were considered as model input parameters for metal speciation assessment. Concentrations of dissolved metals were also used to evaluate their association with the presence of labile-inorganic species in the river water. Detection limits for metals in water samples were Zn: 5.1×10^{-7} mol/l and Pb: 2.4×10^{-13} mol/l. For statistical analysis, annual average concentrations were calculated for each site.

3.2.3. Determination of C_{DGT} in river water

Diffusive Gradients in Thin-films (DGT) devices (DGT Research Ltd, Lancaster, UK) incorporated a Chelex metal binding layer, a 0.8 mm thick diffusive hydrogel (polyacrylamide gel crossed by agarose cross-linker) and a polyethersulphone filter membrane. DGT devices were subject to minimal handling and transported to and from the site in acid cleaned zip-lock bags. A total of 121 DGT measurements were performed bimonthly from December 2013 to November 2014 across the sampling sites as part of the water sampling surveys. Deployment time averaged approximately one month but varied from 18 days to 43 days. Duplicate devices were deployed at two of the sixteen sites and a field blank was processed in the field once per visit. All DGTs were processed in the laboratory within 24 hours: this involved separating the layers of the probe using acid-washed Teflon tweezers. Each resin gel (Chelex) layer was placed in a 2 ml polypropylene tube with 0.7 ml of 1 M HNO_3 (ARISTAR) then stored at 4°C. Immediately before ICPMS analysis, the eluent was diluted 10x with Milli-Q water (18.2 MΩ·cm).

Labile metal concentrations were determined following the method of Zhang and Davison (1995). First, the mass of metal (M) in the Chelex resin is calculated (Eq. 1), where C_e is the concentration of metals in the 1 M HNO_3 elution solution (in μg/l) provided by the ICPMS analysis, V_{gel} is the volume of the resin gel, V_{HNO3} is the volume of HNO_3 added to the resin gel, and f_e is the elution factor for each metal, typically 0.8. Once mass is determined, the concentration of labile metals (C_{DGT}) can be calculated as per Zhang and Davison (1995) (Eq. 2), where, M is the mass of metal in the Chelex resin, Δg is the thickness of the diffusive gel (0.8 mm) plus the thickness of the filter membrane (0.13 mm), D is the diffusion coefficient of metal in the gel established by http://www.dgtresearch.com/, t is deployment time and A is the exposure area (3.14 cm^2).

$$M = (C_e\ (V_{gel}+V_{HNO3})/f_e)/1000 \qquad (1)$$

$$C_{DGT} = (M\Delta g/(DtA))/1000 \qquad (2)$$

3.2.4. Speciation modelling using Windermere Humic Aqueous Model (WHAM/Model VII)

WHAM/Model VII calculates the chemical speciation of metals using humic (HA) and fulvic acids (FA) as active DOM components. In this study, default model parameters were used together with the measurements for the following inputs; temperature, pH, dissolved anions (Cl^-, SO_4^{2-}, NO_3^- and PO_4^{3-}), dissolved metals (Zn^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Fe^{3+}, and Al^{3+}), dissolved inorganic carbon (DIC; input as carbonate) and DOC. For the modelling DOM was assumed to be composed of 50% carbon and the active fraction considered to be 65% fulvic acid, and hence was calculated from DOC values (FA = DOC × 1.3) (Tipping et al., 2008). The activity of both Al and Fe was calculated from the measured total filtered concentration and from the equations derived for Al by Tipping (2005) and for Fe by Lofts and Tipping (2011), with the lower of the two values being adopted. This avoids over-estimation of Al or Fe activity in filtrates containing colloidal forms of the metals. Two different scenarios were considered for modelling. Firstly, Al and Fe oxide precipitates were not considered to be active with respect to surface chemistry. In a second scenario it was considered that the oxides contain active

binding sites and that one mole of oxide has 90 g/mol for Fe (Dzombak and Morel, 1990), and 61 g/mol for Al (Lofts, 2012) of active phase. Concentrations of metals bound to oxides were calculated from the output data. These scenarios were applied to allow comparison with the DGT results.

3.2.5. Estimating metal mixture toxicity using WHAM-F_{TOX}

WHAM-F_{TOX}, a parameterised version of WHAM established by Stockdale et al. (2010) was applied to evaluate the combined impact of protons (H^+) and metals (Al^{3+}, Zn^{2+}, Pb^{2+} and Cu^{2+}). In WHAM-F_{TOX}, the metal toxicity function (F_{TOX}) is considered a product of toxic cation-bound concentrations (ν, mmol/g) and the toxicity coefficient of each analyte (α) and *i* refers to each toxic cation (Eq. 3).

$$F_{TOX} = \Sigma\ \alpha_i\ \nu_i \qquad (3)$$

Concentrations of ν_i were obtained from the WHAM/Model VII modelling as described above without active oxides and with the addition of 10^{-6} g of colloidal humic acid. Toxicity coefficients for aluminium (α_{Al}: 2.24), zinc (α_{Zn}: 2.69), lead (α_{Pb}= 2.51) and hydrogen (α_H:1) were adopted from Stockdale et al. (2010). The Pb toxicity coefficient (α_{Pb}= 2.51, p-value= 0.91) was used in absence of an alternative published value (Stockdale et al., 2010). We suggest the application of α_{Pb} with caution as it may be conservative compared with others Pb toxicity coefficients reported for trout species (cutthroat trout, α_{Pb}=6.7; rainbow trout, α_{Pb}=4.6) (Tipping and Lofts, 2015).

3.2.6. Water quality assessment tools

Tools with different level of complexity were applied to assess the potential harm from dissolved metals to aquatic organisms. Firstly, water hardness was calculated at each sampling point for applying established metal limits under hardness-based standards (http://evidence.environment-agency.gov.uk/). A risk characterization ratio (RCR) was estimated dividing the dissolved metal concentrations or Predicted Effect Concentration (PEC) by the calculated hardness-based limits or No Predicted Effect Concentrations (PNEC). Water quality standards were exceeded (i.e., over accepted limits) if RCR≥1

(RCR=PEC/PNEC). Secondly, the bioavailability assessment tools (BATs) based on the BLM were applied (http://www.wfduk.org/). An alternate risk characterisation ratio (RCR) was calculated, where PEC values are the dissolved metal concentrations, and PNEC are the site-specific values obtained from Biotic ligand models (Zn-BLM and the Pb-BLM-Species Sensitivity Distribution-normalization tool), if RCR≥1 water quality standards were exceeded (Merrington G., 2009; WFD-UKTAG, 2014). For these calculations, Zn-BAT considered dissolved concentrations and water chemical parameters such as Ca^{2+}, pH and DOC as input data. In the case of the Pb-SSD-normalization tool, it required additional parameters like Mg^{2+}, Na^{+}, K^{+}, SO_4^{2-}, Cl^{-}, CO_3^{2-}. Thirdly, the model WHAM-F_{TOX} derived from WHAM/Model VII was applied to predict the effect of water chemistry on the maximum species richness ($SR_{EPT\text{-}max}$). For these calculations, the following conditions were applied: i) if F_{TOX} is lower than 2.33 ($F_{TOX\text{-}LT}$) the maximum SR_{EPT} will be 23 and no toxicity occurs (Eq. 4), ii) a graded linear toxic response occurs as F_{TOX} increases (Eq. 5), and iii) if F_{TOX} is higher than 5.20 ($F_{TOX\text{-}UT}$) no species are predicted to be present (Eq. 6). Obtained values were converted to a percentage of the maximum SR_{EPT} (90% percentile). A detailed description of these calculations is provided by Stockdale et al. (2010).

If $F_{TOX} \leq F_{TOX\text{-}LT}$, then $SR_{EPT} = SR_{EPT\text{-}max}$ *(4)*

If $F_{TOX} > F_{TOX\text{-}LT}$, then $SR_{EPT} = SR_{EPT\text{-}max} - \left(SR_{EPT\text{-}max} \times \frac{F_{TOX} - F_{TOX\text{-}LT}}{F_{TOX\text{-}UT} - F_{TOX\text{-}LT}} \right)$ *(5)*

If $F_{TOX} > F_{TOX\text{-}UT}$, then $SR_{EPT} = 0$ *(6)*

3.2.7. Biological survey

A macroinvertebrate survey was carried out at all sites in August 2014. Samples were collected using a standard kick sampling technique and modified from the Water Framework Directive compliant methodologies (EU-STAR project, 2004). Given the small size of watercourses in the survey, one-minute kick samples were taken at thirteen sites, 30 second was taken at 2 narrow sites and one sweep

sample was taken in a pond at the top of the catchment. Kick samples were followed by a stone search to collect organisms attached to the substrate. Specimens were analysed live at each site. Several were preserved and taken back to the lab for identification confirmation. Invertebrates were analysed to family level. All relevant families within the sample were scored on a presence or absence basis and frequency scale, using the Biological Monitoring Working Party (BMWP) index which rates invertebrates based on their tolerance to organic pollution. BMWPs greater than 100 are associated with unpolluted streams, while the scores of heavily polluted streams are less than 10. In addition, the average sensitivity of the macroinvertebrate families known as the Average Score Per Taxon (ASPT) was determined by dividing the BMWP scores by the number of taxa present. Scores for ASPT are considered from 0 to 10, where 10 indicates an unpolluted site containing large numbers of high scoring taxa (Armitage et al., 1983) (Table 3.1).

Table 3. 1. Scale of water quality categories based on BMWP and ASPT scores.

BMWP score	ASPT score	Water Category	Interpretation
0-10		Very poor	Heavily polluted
11-40	<4	Poor	Polluted or impacted
41-70	>4	Moderate	Moderately impacted
71-100	>5	Good	Clean but slightly impacted
>100	>6	Very good	Unpolluted, un-impacted

3.3. Results

General water chemistry for Hebden Beck has been reported in detail by Valencia-Avellan et al. (2017). It is dominated by the underlying geology of the catchment (i.e. buffered with high Ca and circumneutral pH values), whilst metal levels are associated with the weathering and erosion of Pb and Zn minerals exposed by past mining. Mine-impacted water is characterised by circumneutral pH (6.3-7.5) and elevated metal concentrations. Maximum concentrations of Pb, Cd, Zn, and Cu were detected in site H12 (1.4×10^{-6}, 4.18×10^{-7}, 6.5×10^{-5}, 3.12×10^{-7} mol/l, respectively). Considering the significantly higher concentrations of Zn and Pb, we focus primarily on these metals. Associations between DIC/DOC, sulphate and metals were identified. DIC was strongly correlated with Ca and Mg ($r= 0.9$; $p < 0.001$), whilst DOC was more closely correlated with levels of Fe, Al,

Pb and Cu ($0.1 \geq r \leq 0.7$; $p < 0.003$). Sulphate correlated strongly with zinc and cadmium ($r = 0.6, 0.7$; $p < 0.001$), possibly associated with the dissolution of sulphide minerals (Appendix 2.3).

3.3.1. Dynamic metal (C_{DGT}) concentrations

From DGT measurements at each site, annual average Zn-C_{DGT} concentrations ranged from 2.8×10^{-5} to 4.8×10^{-9} mol/l and for Pb-C_{DGT} from 1.1×10^{-7} to 1.1×10^{-10} mol/l. Highest Zn-C_{DGT} was identified in perennial tributary H7 (2.8×10^{-5} Zn mol/l). Maximum Pb-C_{DGT} (1.1×10^{-7} Pb mol/l) was detected in ephemeral tributaries (H13 and H12) while in the main channel highest concentrations were observed in H6 (7.5×10^{-6} Zn mol/l) and H10 (2.3×10^{-8} Pb mol/l) (Table 3.2).

Table 3. 2. Annual averages and standard deviation (±SD) of dissolved metals (M_D)in water samples (mol/l), metal concentrations from DGT devices-C_{DGT} (mol/l) and exceedances of Environmental Quality Standards (EQS) by comparing different tools EQS-H (a), EQS-B and WHAM-F_{TOX} (%SR_{EPT}) for assessing effects of Zn and Pb pollution RCR: Risk Characterisation Ratio, PEC: Predicted Effect Concentration/ PNEC: Predicted No Effect Concentration.

Sites	Description	Zn_D-measured (mol/l)	Zn-C_{DGT} (mol/)	Zn *RCR*		Pb_D-measured (mol/l)	Pb-C_{DGT} (mol/l)	Pb RCR		WHAM-F_{TOX}
				EQS-H	*EQS-B*			*EQS-H*	*EQS-B*	%SR_{EPT}
H15	Reservoir	3.1×10^{-5} ($\pm7.2\times10^{-6}$)	1.2×10^{-5} ($\pm6.9\times10^{-6}$)	253.5	54.0	1.3×10^{-6} ($\pm4.0\times10^{-7}$)	5.7×10^{-8} ($\pm5.2\times10^{-8}$)	38.8	8.5	43
H14	PT	2.1×10^{-5} ($\pm5.2\times10^{-6}$)	1.5×10^{-5} ($\pm4.4\times10^{-6}$)	174.7	45.9	7.6×10^{-7} ($\pm3.6\times10^{-7}$)	6.1×10^{-8} ($\pm1.9\times10^{-8}$)	21.9	6.8	55
H13	ET	3.2×10^{-6} ($\pm6.3\times10^{-6}$)	6.1×10^{-7} ($\pm3.2\times10^{-7}$)	25.9	4.1 (b)	9.9×10^{-7} ($\pm2.6\times10^{-7}$)	1.1×10^{-7} ($\pm6.6\times10^{-8}$)	28.6	1.1 (d)	52
H12	ET	6.5×10^{-5} ($\pm3.0\times10^{-5}$)	2.7×10^{-5} ($\pm4.0\times10^{-6}$)	85.0	117.6	1.4×10^{-6} ($\pm4.4\times10^{-7}$)	1.1×10^{-7} ($\pm4.0\times10^{-8}$)	39.5	17.1	66
H11	PT	6.3×10^{-6} ($\pm2.1\times10^{-5}$)	3.3×10^{-6} ($\pm7.6\times10^{-6}$)	51.3	8.7	1.5×10^{-7} ($\pm4.5\times10^{-7}$)	9.2×10^{-9} ($\pm1.8\times10^{-8}$)	4.4	0.8	85
H10	MC	6.8×10^{-6} ($\pm2.8\times10^{-6}$)	5.2×10^{-6} ($\pm2.5\times10^{-6}$)	55.6	11.1	3.8×10^{-7} ($\pm2.0\times10^{-7}$)	2.3×10^{-8} ($\pm1.5\times10^{-8}$)	11.2	2.9	82
H9	PT	1.5×10^{-6} ($\pm1.9\times10^{-6}$)	1.3×10^{-6} ($\pm5.5\times10^{-7}$)	12.0	2.1 (b)	1.0×10^{-7} ($\pm1.1\times10^{-7}$)	4.6×10^{-9} ($\pm4.4\times10^{-9}$)	2.9	0.5	77
H8	PT	4.1×10^{-6} ($\pm1.5\times10^{-6}$)	3.9×10^{-6} ($\pm2.3\times10^{-6}$)	3.6	7.4	9.2×10^{-8} ($\pm3.2\times10^{-8}$)	1.1×10^{-8} ($\pm1.1\times10^{-8}$)	2.6	1.1	100
H7	PT	4.9×10^{-5} ($\pm1.3\times10^{-5}$)	2.8×10^{-5} ($\pm8.5\times10^{-6}$)	42.9	209.2	2.1×10^{-8} ($\pm6.1\times10^{-8}$)	1.2×10^{-9} ($\pm1.1\times10^{-9}$)	0.6	1.7	76
H6	MC	7.8×10^{-6} ($\pm1.5\times10^{-6}$)	7.5×10^{-6}($\pm1.0\times10^{-6}$)	10.2	12.8	2.4×10^{-7} ($\pm9.9\times10^{-8}$)	8.5×10^{-9} ($\pm4.4\times10^{-9}$)	6.9	1.7	88
H5	PT	1.3×10^{-5} ($\pm2.9\times10^{-6}$)	1.3×10^{-5} ($\pm1.5\times10^{-6}$)	11.6	43.9	2.6×10^{-7} ($\pm2.2\times10^{-7}$)	4.9×10^{-8} ($\pm1.8\times10^{-8}$)	7.5	8.7	100
H4	ET	5.5×10^{-7} ($\pm1.4\times10^{-7}$)	2.6×10^{-7} ($\pm8.9\times10^{-8}$)	4.5	2.5 (b,c)	2.1×10^{-8} ($\pm8.2\times10^{-9}$)	3.7×10^{-9} ($\pm5.4\times10^{-10}$)	0.6	0.02 (d)	35
H3	PT	$<5.1\times10^{-7}$	1.2×10^{-6} ($\pm5.1\times10^{-8}$)	0.2	0.8	8.0×10^{-10} ($\pm9.5\times10^{-10}$)	5.4×10^{-10} ($\pm4.1\times10^{-10}$)	0.02	0.1	100
H2	MC	7.4×10^{-6} ($\pm1.1\times10^{-6}$)	7.0×10^{-6} ($\pm1.0\times10^{-6}$)	9.7	17.7	1.9×10^{-7} ($\pm1.4\times10^{-7}$)	1.3×10^{-8} ($\pm3.9\times10^{-9}$)	5.5	2.3	97
H1P	PT	5.6×10^{-7} ($\pm1.1\times10^{-6}$)	4.8×10^{-9} ($\pm4.5\times10^{-9}$)	0.7	2.4	3.5×10^{-9} ($\pm3.1\times10^{-9}$)	1.1×10^{-10} ($\pm3.0\times10^{-11}$)	0.3	0.1	100
H1	MC	2.4×10^{-6} ($\pm1.1\times10^{-6}$)	2.5×10^{-6} ($\pm6.6\times10^{-7}$)	2.1	4.2	8.0×10^{-8} ($\pm6.6\times10^{-8}$)	3.7×10^{-9} ($\pm3.3\times10^{-9}$)	2.3	1.0	100

(a) Limits of EQS based on site-specific hardness, Zn.EQS-H= 1.3×10^{-7} (for sites H15, H14, H13, H11, H10, H9, H4); 7.6×10^{-7} (for sites H12, H6, H2, H1P) and 1.2×10^{-6} (for sites H8, H7, H5, H3, H1). Pb.EQS-H= 3.5×10^{-8} for all sites.
(b) pH values were outside the limits of Zn-BAT tool. Default limit (pH=6) was applied for Zn.EQS-B calculations.
(c) Ca concentrations were outside the limits of Zn-BAT tool. Default limit (Ca=3 mg/l) was applied for Zn.EQS-B calculations.
(d) pH values were outside the limits of Pb-SDD tool (pH=6=8.5). Pb-PNEC should be interpreted with care.

3.3.2. Comparison between dissolved metal concentrations and C_{DGT} measurements

DGT measurements were compared with the mean of metal concentrations in water samples calculated from deployment and retrieving dates (Appendix 3.1). Figure 3.2 shows the linear correlations between measured dissolved metals in water samples and metals measured by DGT (M-C_{DGT}). A strong relationship exists between Zn measured dissolved species and Zn-C_{DGT} (R^2=0.75, p<0.001). For Pb, a moderate relationship was observed between dissolved concentrations and C_{DGT} (R^2=0.59, p<0.001). Whilst there is correlation between C_{DGT} and dissolved concentrations there is a lesser degree of agreement, as indicated by the slopes of 0.46 (Zn) and 0.07 (Pb) (Figure 3.2).

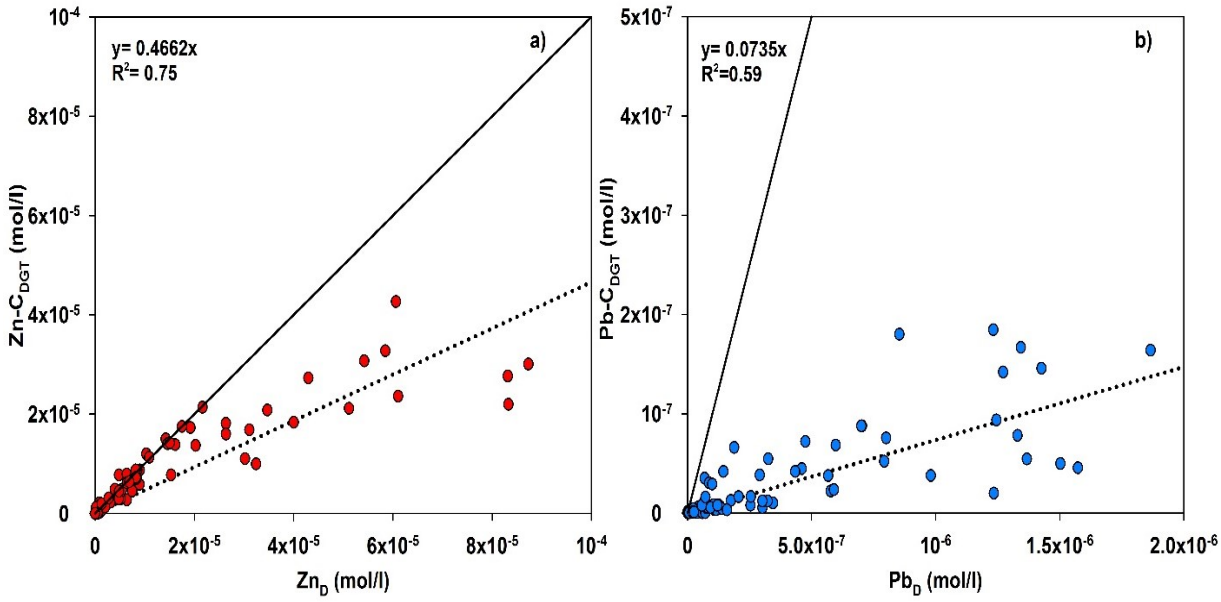

Figure 3. 2. Measured dissolved metals versus DGT concentrations (C_{DGT}). Panel a, shows the correlation between Zn_D and Zn-C_{DGT}. Panel b, shows the correlation of Pb_D with Pb-C_{DGT}. Dotted lines represent a regression line, solid lines represent the ideal 1:1 line.

3.3.3. Metal speciation calculated by WHAM/Model VII

Modelling where oxide precipitates are not surface active

Concentrations of predicted organic and inorganic species of Zn, and Pb are shown in Figure 3.3. Average concentrations of metal-organic complexes (i.e. metal-fulvic acid complexes) were higher for Zn than Pb, although as a function of total dissolved metal, Pb had a greater relative amount present as organic complexes than Zn. Values ranged for Zn from 2.9×10^{-8} to 1.2×10^{-5} mol/l and for Pb from 2.0×10^{-10} to 1.1×10^{-6} mol/l, highest values were in sites H11 and H15 respectively. Similar pattern was observed for inorganic species; higher average concentrations occurred for Zn (3.6×10^{-7} to 5.8×10^{-5} mol/l), and lower for Pb (6.0×10^{-10} to 7.2×10^{-7} mol/l), with the highest concentrations in sites H12 and H13. Figures 3.4a and 3.4c show linear correlation between dissolved inorganic metal species predicted by WHAM and C_{DGT} measurements of Zn and Pb. Good correspondence was observed for Zn (R^2= 0.81, $p<0.001$) and moderate relationship for Pb (R^2=0.54, $p<0.001$).

Modelling where oxide precipitates are surface reactive

Precipitation of Fe and Al oxides (with reactive surface) were simulated by using the concentration of precipitated metal to the mass of active phase (Figures 3.4b-3.4d). Similar correlations were obtained when oxides were not surface reactive Zn (R^2= 0.81, $p<0.001$) and Pb (R^2= 0.51, $p<0.001$). The presence of colloidal Pb was estimated showing more affinity to FeOx than AlOx. Concentrations of Pb-FeOx complexes ranged from 5.7×10^{-11} to 2.5×10^{-7} mol/l, while Pb-AlOx complexes from 6.8×10^{-12} to 2.5×10^{-8} mol/l. For both complexes highest concentrations were identified in H12 (Figure 3.5).

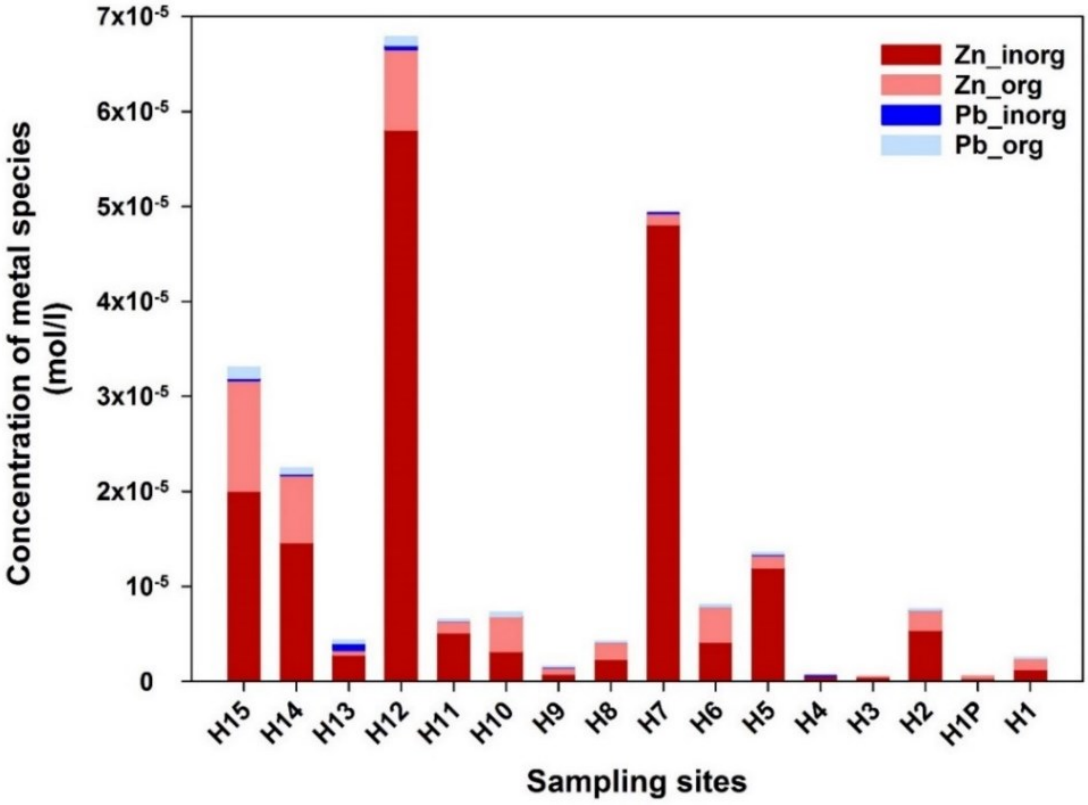

Figure 3. 3. Calculated concentrations of metal species in the absence of surface active oxide precipitates using WHAM/Model VII.

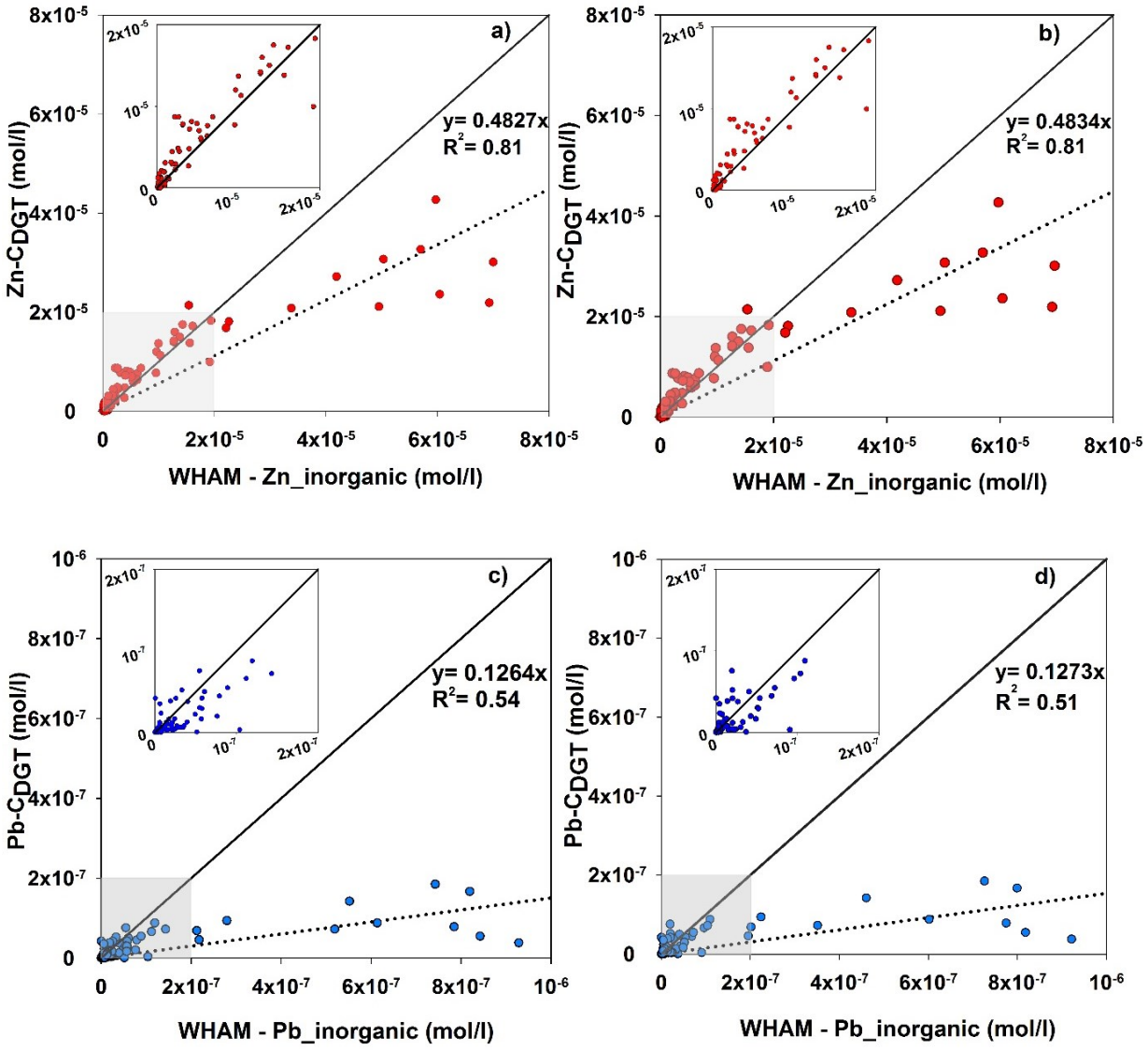

Figure 3. 4. Relationship between inorganic metal concentrations (mol/l) calculated by WHAM and metal concentrations from C_{DGT} measurements (mol/l) for Zn (panels a and b) and Pb (panels c and d). Inorganic concentrations were predicted in WHAM in the absence (panels a and c) and presence (panels b and d) of active oxides. Dotted lines represent a regression line and solid lines represent the ideal 1:1 line. The inset graphs show the agreement at concentrations below 2×10^{-7} (mol/l) between inorganic metal concentrations calculated by WHAM and metal concentrations from C_{DGT} measurements.

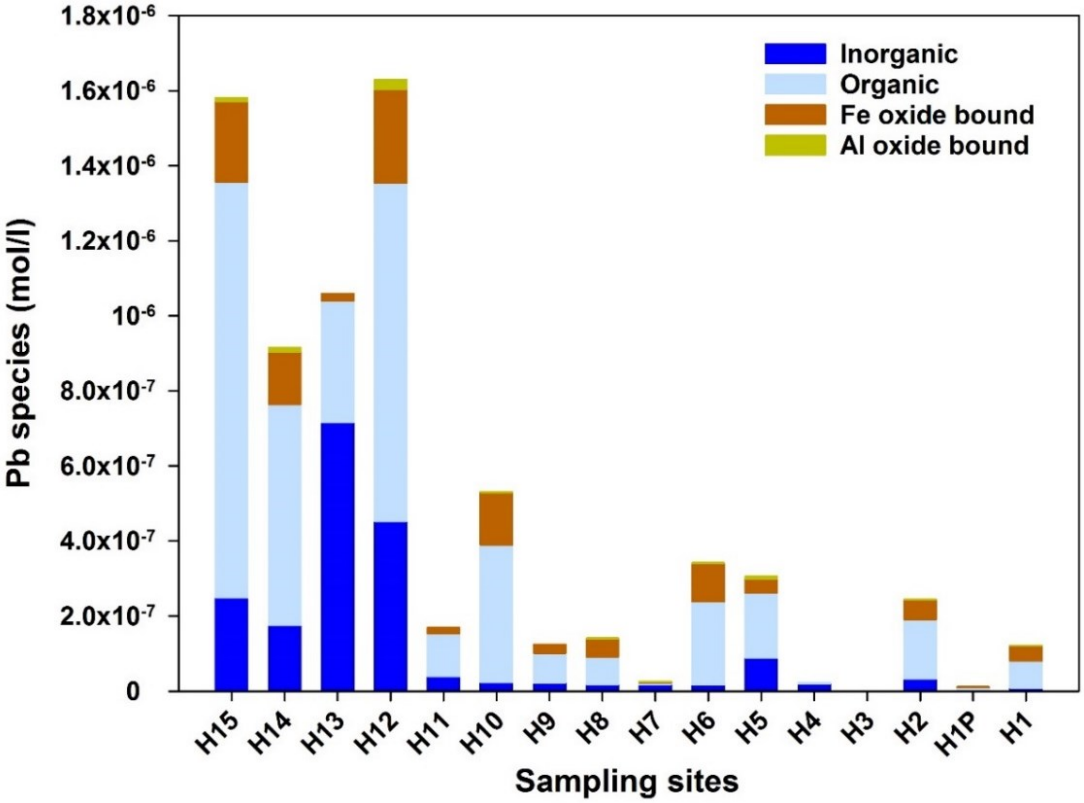

Figure 3. 5. Calculated concentrations of Pb species in the presence of surface active oxide precipitates using WHAM/Model VII.

3.3.4. Water quality and ecotoxicological assessment

Environmental Quality Standards: EQS-H and EQS-B

Annual average concentrations were used for assessing EQS-H and EQS-B. The EQS-H standards were exceeded for Zn from 0.2 to 253.5-fold and for Pb from 0.02 to 39.5-fold (Table 3.2). Highest Zn exceedances (>60-fold) occurred in sites H15, H14 and H12; these sites and H13, also presented highest Pb exceedances (>20-fold). The EQS-B standards were exceeded for Zn from 0.8 to 209.2-fold and for Pb from 0.02 to 17.1-fold. Highest Zn exceedances (>50-fold) appeared in sites H7>H12>H15. For Pb, highest levels (>6-fold) were presented in H12>H5, H15>H14 (Table 3.2).

3.3.5. Toxicity function: WHAM-F_{Tox}

Concentrations of metals bound to humic acid are shown in Figure 3.6. Concentrations of metals bound to humic acid ranged for Zn (0.0013 to 0.9 mmol/g) and Pb (0.0001 to 0.09 mmol/g) (Figure 3.6). Sites H15, H14, H12, and

H7 were characterised by high Zn concentrations (≥0.5 mmol/g), the same sites (except for H7) presented high Pb concentrations (≥0.05 mmol/g).

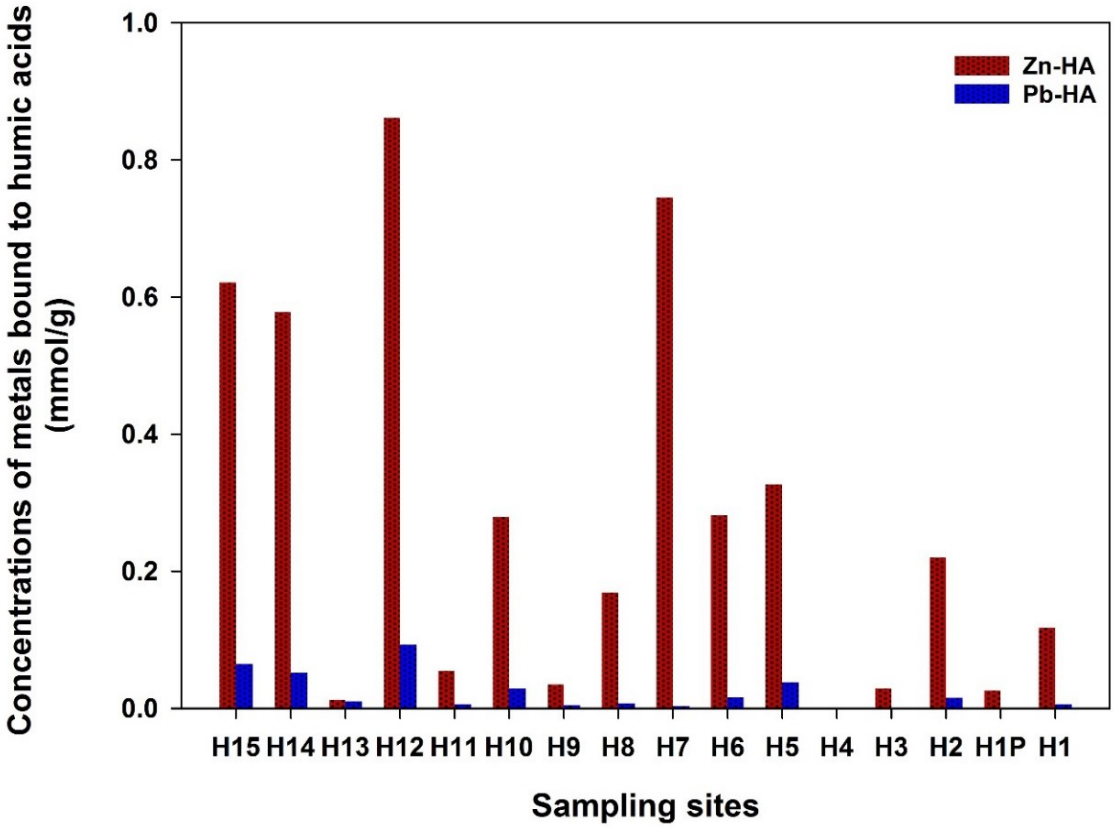

Figure 3. 6. Calculated concentrations of Zn and Pb bound to humic acids (mmol/g).

Toxicity contributions ($F_{TOX\text{-}M}$) for each element (Zn, Pb, H and Al) were calculated from Equation 3 (Methods section) and summed to produce a total toxicity function value (Total_F_{TOX}). Equations 4 and 6 were applied to convert Total_F_{TOX} to a prediction of the maximum species richness that could be expected based on the chemistry of each stream. Effects of metal mixtures on predicted species richness are shown in Table 3.3. Reduction of predicted species richness (SR_{EPT} <23) was identified at several sites. In sites H11, H10, H6 and H2 a slight decrease was presented (SR_{EPT}: 22 to 19) associated with the combined moderate toxicity of H, Zn and Al, a major decrease (SR_{EPT}: 18 to 10) was shown in sites H15, H14, H13, H12, H9 and H7 due to higher contributions from Zn, contributions of H and Al and additionally small contributions from Pb; while the lowest value (SR_{EPT}: 8) occurred in site H4 related to the influence of H and Al and not metals.

Table 3. 3. Predicted species richness of macroinvertebrates orders (Epemeroptera, Plecoptera and Trichoptera) (SR_{EPT}). Toxicity values (F_{TOX}) obtained by WHAM-F_{TOX} were calculated from monthly data. Values are expressed as mean and standard deviation (±SD).

Sites	$SR_{(EPT)}$	Total_F_{TOX}	$F_{TOX\text{-}Zn}$	$F_{TOX\text{-}Pb}$	$F_{TOX\text{-}H}$	$F_{TOX\text{-}Al}$
H15	10	4.0	1.7(±0.7)	0.2(±0.1)	1.4(±0.4)	0.4(±0.5)
H14	13	3.6	1.6(±0.5)	0.1(±0.0)	1.2(±0.3)	0.3(±0.5)
H13	9	4.1	0.0(±0.1)	0.0(±0.0)	2.6(±0.3)	1.4(±0.3)
H12	15	3.3	2.3(±0.9)	0.2(±0.1)	1.0(±0.3)	0.2(±0.5)
H11	20	2.8	0.1(±0.3)	0.0(±0.0)	1.8(±0.6)	0.3(±0.2)
H10	19	2.8	0.7(±0.3)	0.1(±0.0)	1.2(±0.4)	0.1(±0.1)
H9	18	3.0	0.1(±0.1)	0.0(±0.0)	2.0(±0.7)	0.4(±0.2)
H8	23	1.7	0.5(±0.2)	0.0(±0.0)	0.9(±0.3)	0.1(±0.1)
H7	18	3.0	2.0(±0.3)	0.0(±0.0)	1.0(±0.2)	0.0(±0.1)
H6	20	2.7	0.8(±0.2)	0.0(±0.0)	1.2(±0.3)	0.2(±0.3)
H5	23	2.3	0.9(±0.2)	0.1(±0.1)	1.1(±0.2)	0.1(±0.2)
H4	8	4.2	0.0(±0.0)	0.0(±0.0)	3.3(±0.4)	0.9(±0.3)
H3	23	1.2	0.1(±0.0)	0.0(±0.0)	1.0(±0.3)	0.0(±0.1)
H2	22	2.4	0.6(±0.2)	0.0(±0.0)	1.3(±0.4)	0.2(±0.3)
H1P	23	1.9	0.1(±0.0)	0.0(±0.0)	1.5(±0.6)	0.2(±0.1)
H1	23	1.5	0.3(±0.0)	0.0(±0.1)	0.8(±0.2)	0.0(±0.1)

Contributions of metal toxic effects (F_{TOX}) at different pH conditions were predicted by WHAM-F_{TOX} (Figure 3.7). Figure 3.7a demonstrates the effects of heavy metals at spoil runoff or adit sites**,** higher toxicity (>2.3) is related to acidic waters (H4 and H13), while adits or water draining through spoil sites are rich in Zn and Pb (H15, H14, H12, H7). Figure 3.7b highlights the lack of metal contribution of metals at the lower pH sites (pH<5) due low metal-humic binding as a result of enhanced competition for binding sites from the elevated concentrations of H^+ and Al (likely present as oxides) or possible lower metal too.

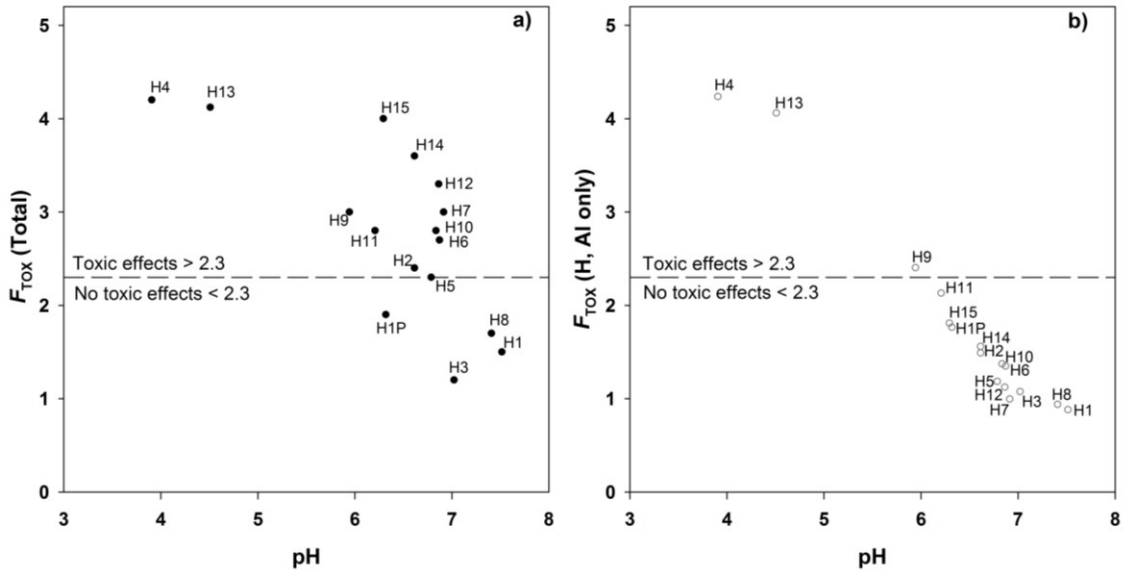

Figure 3. 7. Variations of toxicity function (F_{TOX}) with pH. Panel a shows total F_{TOX}, which includes the effect of metals derived from mine-affected areas and acid contribution from peat soils. Panel b shows the contribution of only H and Al to F_{TOX}. The horizontal dashed line represents the F_{TOX} threshold (2.3), above which toxic effect are predicted to occur. The upper limit of the plot represents the upper threshold (5.2).

3.3.6. Evaluation of metal assessment tools

EQS-H, EQS-B and WHAM-F_{TOX} were compared to evaluate their levels of protection with respect to metal toxicity in aquatic ecosystems (Table 3.2). From the comparison, EQS-H are more conservative than EQS-B. EQS-H showed wider ranges of exceedance for Zn (0.2 to 253.5-fold) and for Pb (0.02 to 39.5-fold), while EQS-B showed narrow ranges for Zn (0.8 to 209.2-fold) and Pb (0.02-17.1-fold). For both tools, sites H15, H14, H12 and H7 showed the highest Zn failures. For Pb same sites, except H7 showed major failures, in addition, H13 showed exceedance by using EQS-H and H5 with EQS-B. Calculations from WHAM-F_{TOX} showed that at eleven sites the water chemistry may reduce the maximum species diversity of macroinvertebrates by between 65 and 3%. Sites H12, H13, H14, H15 and H4 showed the largest predictions for reductions in species richness, with reductions from 65 to 34%.

3.3.7. In situ macroinvertebrate survey

A total of twenty four macroinvertebrate families were identified across all of the sites. The BMWP scores based on the presence and absence of macroinvertebrates families indicated a moderately impacted water quality

(BMWP>50) for sites H14, H10, H9, H6, H5, H3, H2, H1P and H1, while lower scores (BMWP<25) in sites H15, H13, H12, H11, H8, H7 and H4 indicated pollution deriving poor water quality (Appendix 3.2), while ASTP scores (<2) showed sites H13 and H12 as the most polluted (Appendix 3.3). In addition, four macroinvertebrate orders were predominant in the catchment (Appendix 3.4). Based on numbers of individuals, the order Diptera showed 39.5% represented by the families Psychodidae and Simuliidae (Appendix 3.5), followed by the orders Ephemeroptera (mayfly) with 28.1% where Baetidae was the most prevalent (Appendix 3.6), Trichoptera (caddisfly) presented 17.9% with Hydropsychidae as the dominant family (Appendix 3.7), and the order Plecoptera (stonefly) with 11% represented by the family Perlodidae (Appendix 3.8).

3.4. Discussion

For aquatic environments, metal assessment has evolved as bioavailability is increasingly considered a critical measure for improving water quality, e.g. under the EU Water Framework Directive. A preliminary water quality assessment was carried out where dissolved concentrations of Zn and Pb were assumed to be bioavailable depending on ranges of water hardness conditions, and exceedances were calculated from previous-established EQS-H. Concentrations of Zn and Pb exceeded the limits by 174.7-fold and 39.5-fold respectively, however the implications for their bioavailability were unclear. Merrington (2016) has indicated that hardness limits have been derived from ecotoxicological tests mainly from crustaceans and fish, where water chemical parameters do not necessarily reflect field conditions. Thus, the use of hardness-based standards may be overly conservative as they might under-represent other important taxa. In addition, they fail to consider chemical speciation in distinguishing sites with potential environmental risk associated with metals.

In complex environments such as freshwaters, understanding of the underlying conditions controlling the dynamics and speciation of metals is critical for assessing and managing the risk they pose to aquatic life (Han et al., 2013). This study evaluated the utility of DGT for yielding both time averaged and dynamic Zn and Pb concentrations (potentially a proxy for organism availability) (Diviš et

al., 2007; Degryse et al., 2009; Amato et al., 2014; Søndergaard et al., 2011; 2014; Omanović et al., 2015). By comparing DGT measurements (C_{DGT}) with direct water measurements (M-measured), results indicated that C_{DGT} concentrations were generally lower than the directly measured values. For Zn-C_{DGT} and Zn-measured a strong linear correlation (R^2=0.75) was present suggesting the presence of Zn mainly as free ions and readily labile complexes, a slope of 0.47 revealed that DGT measurements at higher concentrations failed to reflect dissolved measured concentrations. This might be caused by the kinetic rate of Zn forms, which will determine its accumulation into the resin layer (Warnken et al., 2007). Free Zn^{2+} seems to be rapidly absorbed by the resin layer, while the supply of labile complexed forms will depended on their degree of lability (Puy et al., 2012). Zhang and Davison (2015) indicated that fully labile complexes might not be completely dissociated within the diffusion layer, thus their uptake in the resin could be reduced or not occur. Correlation between Pb-C_{DGT} and Pb-measured was moderate (R^2=0.59), with a slope of 0.07, possibly attributable to the presence of less labile Pb forms (e.g. Pb-FeOx, Pb-DOM) that need more time for diffusion or presence of bigger particles that could be excluded from DGT membranes (Han et al., 2013). Considering correlations from both metals, C_{DGT} measurements can be affected by the amount of total metal dissolved concentrations present as free ions and their complexation with inorganic or organic substances (Zhang and Davison, 2015). Furthermore, long deployments (>15 days) might expose DGTs to biological factors like biofouling, and flow fluctuations that might decrease the stirring rates, reducing DGT's performance (Davison and Zhang, 1994; Webb and Keough, 2002; Turner et al., 2014).

Metals speciation and bioavailability are controlled by a range of different factors such as pH, ionic strength, DOC, hardness, pH and inorganic or organic colloids. Given these factors, the quantity of metal available for organism uptake is not reflected by the total dissolved concentration (Hart, 1981; Luoma, 2008). This study correlated M-C_{DGT} measurements with inorganic metal complexes predicted from dissolved measured concentrations under the absence and presence of active inorganic colloids (e.g. FeOx and AlOx) as they can compete with Zn and Pb for binding with DOM. By excluding active oxide colloids in the

modelling, Zn is largely present as inorganic rather than organic complexes, and highest predicted inorganic concentration was at site H12 (5.8×10^{-5} mol/l). Conversely Pb had a greater affinity for organic binding, with highest organic concentration at H15 (1×10^{-6} mol/l) (Figure 3.5). Both metals showed good linear correlations between inorganic complexes and C_{DGT} for Zn (R^2=0.81), and Pb (R^2=0.54), reflecting an improved correlation of Zn-C_{DGT} with predicted Zn inorganic complexes than previous correlation between Zn-C_{DGT} with Zn-measured, which can be attributable to the fact that dissolved Zn is present primarily as inorganic and free ions. Outcomes from modelling conditions where oxide precipitates are surface reactive showed similar behaviours for Zn (R^2=0.81) and Pb (R^2=0.51) than obtained in the absence of surface activity. The agreement observed for Zn confirms that the total dissolved Zn (mainly inorganic) is approximately equivalent to the dynamic Zn-C_{DGT} (except at high Zn loading, as previously discussed). For Pb, there is a discrepancy between Pb-C_{DGT} and dissolved Pb due to larger fractions in other less labile phases (Pb-organic complexes) (Warnken et al., 2008; Han et al., 2013). The lack of improved agreement to the inorganic-Pb in presence of oxides with the Pb-C_{DGT} (dynamic) concentration implies that the model may be under-predicting the binding to these forms. However, low concentrations of Pb-inorganic can be associated to the absence of precipitated iron and aluminium oxides, for instance, site H4 showed no precipitation of aluminium oxides and low precipitation of iron oxides, while other sites like H3 and H7 presented very low concentrations of FeOx ($<6.9\times10^{-7}$ mol/l) and AlOx ($<3.3\times10^{-7}$ mol/l). From these results, DGT provides useful information about metal dynamics and speciation which is valuable for understanding metal uptake mechanisms, however current results indicated its inadequacy as a substitute for water measurements due to poor uptake kinetics at higher metal concentrations, limiting an accurate assessment of metal bioavailability. Zhang and Davison (2015) have indicated that given the complexity of biological systems and chemistry of environmental media, the ability of DGT to mimic metal uptake and predict bioavailability is variable. Further research based on the comparison of field data and laboratory experiments under

controlled temperature, deployment time and flow rates are suggested for evaluating the applicability of DGTs regarding metal bioavailability in freshwaters.

Outcomes from EQS-H, EQS-B and WHAM-F_{TOX} provided different levels of prediction regarding metal bioavailability and toxicity. In comparing EQS-H and EQS-B, the simpler approach (EQS-H) is more conservative than the standard that considered more water chemistry parameters and metal-organism interactions (EQS-B) (Merrington, 2016). However, by contrasting EQS-B and WHAM-F_{TOX}, results suggest that the latter approach is the least conservative of the three approaches. This was clearly identified in sites with exceeded EQS-B like H7 (Zn: 209.2-fold and Pb: 1.7-fold) and H5 (Zn: 43.9-fold and Pb: 8.7-fold), but with F_{Tox}-SR showing 100% for predicted species richness for both sites. WHAM-F_{TOX} also revealed that major toxic effects can occur at circumneutral pH mostly due to Zn and Pb.

Moreover, a biological survey agreed with this chemical assessment. The most impoverished sites presented low predicted macroinvertebrate richness (SR_{EPT}=35%) correlating with high concentrations of metals (H12, H13 and H14) or low-pH values (H4) (Table 3.2). Overall, the orders Diptera and Trichoptera were dominant (39.5% and 28.1%) with Chironomidae and Hydropsychidae as the more abundant families. Responses of macroinvertebrates and diatoms to different metal levels in Hebden Beck have been previously evaluated by the UK-Environment Agency (2014). The ecological assessment revealed a direct relationship between increasing Zn concentrations and reduced biodiversity, likewise invertebrate data showed that responses of species composition could be related to the influence of complex interactions between metals and acid scenarios.

In early and current assessment, the family Baetidae (O: Ephemeroptera) was dominant, possibly due to its tolerance to different levels of pollution. A study of Mebane et al. (2015), indicated that the most sensitive species to pollution are the last to re-colonise after recovery from Cu contamination. In our study less sensitive families (Perlodidae, Nemouridae, Baetidae) are widespread throughout the catchment. More sensitive families like Glossomidae,

Ephemerellidae and Heptageniidae are mainly confined to main channel sites (H2, H6, H10), although Heptageniidae was also present in a metal impacted site H14 (predicted species richness of 55% of the theoretical maximum). Another metal sensitive family, Psychodidae was present in less metal impacted sites, such as H1P, showing a predicted species richness of 100%. These results are consistent with the F_{TOX} species predictions, however current interpretations are generalised as we only identified macroinvertebrates to family level, and species sensitivity is complex with differences in pollution tolerance occur within different taxa (Clements et al., 2013).

From a regulatory perspective, bioavailability based standards (EQS-B) offer a better ecologically approach to address water quality failures than traditional hardness corrections (EQS-H) (Peters et al., 2016). In this study, both standards facilitated the screening of sites with potential metal risk, however, EQS-B identified sites where dissolved metal concentrations and speciation mechanisms (M-C_{DGT}) were related.

Although bioavailability-based models have been developed on field data and applied in the establishment of water quality standards for metals, their pertinence to routine regulatory purposes need to be extensively verified, especially for sites where physicochemical conditions (e.g. pH, hardness, DOC) are near or outside of the boundaries of the model (Rüdel et al., 2015; WFD-UKTAG, 2009a). This is the case of EQS-B for zinc. Some of the studied sites presented pH and Ca values below Zn-BLM limits, thus default limits of this tool (pH= 6 and Ca= 3mg/l) were used in Zn assessment, consequently the use of complementary models like WHAM and WHAM-F_{TOX} can offer more complete toxicity predictions under original physico-chemical conditions.

Precisely because WHAM-F_{TOX} considers protons within its formulation, it can be applied to any combination of water chemistry and metal mixtures. For a practical implementation of these tools a compliance scheme has been suggested by the UK Technical Advisory Group which includes: i) comparison of metal concentrations with EQS-H, ii) application of BLM tools (e.g. Zn-BLM, Pb-BLM) to predict site-specific bioavailability (EQS-B), and iii) local refinement using

models that require a larger number of input parameters (e.g. full M-BLM or WHAM-VII) (Bio-met, 2015; WFD-UKTAG, 2009b). Further research is desirable, especially in the generation of toxicity data to improve the significance of toxicity coefficients (e.g. α_{Pb}). Nevertheless, the combination of EQS-B and WHAM-F_{TOX} could provide a rational assessment which is essential for the purposes of considering remediation activities. Vulnerable sites can be prioritised under a holistic scenario (water chemistry, metal concentrations and interactions between metal and organism) where remedial actions can be focused on reducing metal bioavailability for the purpose of improving ecological endpoints.

This study has evaluated different methods for the assessment of the chemical and ecological status of Hebden catchment regarding metal pollution. The first method (EQS-H) was a simple and well-established technique, which provided a very conservative regulatory limit that may be overprotective as seen when calculations are performed with tools designed specifically to account for speciation and organisms interactions. The second (EQS-B) and third (WHAM-F_{TOX}) method based on more rigorous bioavailability tools (e.g. Zn-BLM and Pb-SSD), provided less conservative limits but supported by the normalisation of the ecotoxicity data to the site specific water chemistry. Through the evaluation of these approaches a better understanding of metal speciation and dynamics was possible, supporting the prediction of toxic effects from metal mixtures and the identification of sites with potential biological risks. Furthermore, the biological survey provided a context for relating the response of aquatic organisms to river water chemistry and pollutants, which are useful for future ecological assessments.

3.5. Conclusions

The use of bioavailability-based standards is needed to fully assess the impacts of metal pollution and implement regulatory actions for delivering good ecological status.

- In carboniferous catchments, metal toxic effects occur at circumneutral pH. Zn is mainly present as free ions and readily labile complexes while Pb is present as less labile forms (e.g. organic complexes and colloids).

- Metal assessment through the EQS-H approach is more conservative than EQS-B and WHAM-F_{TOX}. The incorporation of bioavailability will better address some of the processes that control toxic metals effects. In addition, catchment management will be improved as the bioavailability approach will aid in the identification of key reaches where remediation may be required.
- Metal concentrations estimated from DGT provided useful information for the assessment of Zn and Pb speciation and for understanding metal uptake mechanisms. However, discrepancies between M-measured and M-C_{DGT} suggest that further research is required for evaluating the applicability of this tool in the assessment of metal bioavailability under field conditions.

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Chapter 4: Effect of episodic rainfall on aqueous metal mobility from historical mine sites

Invitation to resubmit in Environmental Chemistry

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Abstract

The increasing frequency and magnitude of episodic rainfall events may affect metal mining areas by remobilisation and deposition of metal-rich sediments and enhancing metal-rich run off, impacting river water quality. This study assesses the effects of episodic rainfall in a Carboniferous headwater catchment contaminated by historical Pb and Zn mining. Results suggest that episodic rainfall increases concentrations of dissolved metals, with greater impact on Pb than Zn concentrations, but without altering typical circumneutral conditions of the river. During episodic flow, an ephemeral tributary draining through extensive spoil tips was the major contributor of dissolved metals. Runoff affected the dissolution of secondary metal-carbonate minerals, particularly constraining the dissolution of smithsonite ($ZnCO_3$) due to the abundance of carbonate and bicarbonate derived from bedrock weathering. Toxicity estimations showed that metal concentrations derived from episodic rainfall do not directly correspond to a parallel increase in predicted toxicity, highlighting the complexity in chemical speciation changes during episodic rainfall events.

4.1. Introduction

Changes in climate impact the hydrological cycle. Extreme events like droughts and floods may have significant impacts on the quantity and quality of waterbodies, with direct or indirect effects on ecosystems (Hrdinka et al., 2012; Park et al., 2011; Foulds et al., 2014). In river systems, headwaters streams, ephemeral ponds and ditches are most sensitive to climatic changes since severe alterations in temperature and precipitation could affect evapotranspiration, flow, soil moisture and groundwater recharge (Whitehead et al., 2009; Ayers et al., 1994; Chapman et al., 1993). Floods can be effective agents of contaminant dispersal by triggering primary pollution or remobilisation of deposited material (Miller et al., 1998). Primary pulses are produced by major rainstorms after periods of extended drought, when soluble salts concentrated on the surface of mine wastes and spoils are quickly dissolved and flushed into receiving surface waters (Nordstrom, 2011). Runoff from watersheds draining metal mining areas is considered an acute problem as exposed tailings produce metal-rich overflow that is often redistributed downstream (Myers et al., 1985; Förstner and Wittmann, 2012). Once in sediments, metals can remain in floodplains for decades to centuries until their remobilisation by erosion, creating a long-lived contamination problem (Ciszewski and Grygar, 2016).

In the UK, the floods of autumn 2000 provided clear evidence of the potential effects of climate change on diffuse pollution in formerly mined river catchments (Dennis et al., 2003; Macklin et al., 2006). The excessive flux of metals generated by the legacy of metal mining has significantly increased the levels of metal pollution in many catchments (Mayes et al., 2010). Consequently, these catchments represent a challenge in achieving “good ecological and chemical status” as required by the EU Water Framework Directive (WFD) or other national legislation. In addition to climate influenced factors, the dispersal of metals depends on the dynamics of each catchment (Miller, 1997). For example, where rivers flow over limestone bedrock the pH is buffered, exerting controls over mineral solubility, metal transport and bioavailability (Valencia-Avellan et al., 2017). However, this buffering capacity can be slowly consumed by rainfall (e.g. acid rain) producing shifts in the pH, allowing desorption of metals from sediments

or soils (Salomons, 1995). Mitigating the impact of metals on water quality requires knowledge of the biogeochemistry of metal in solid and solution phases, as well as a local understanding of major sources of pollutant metals (Lambing et al., 2004; Wirt et al., 1999; Sandén et al., 1997; Nieto et al., 2007; Park et al., 2011).

The limited primary data about episodic high rainfall make difficult the understanding of their effects on metal dynamics. This study seeks to address this knowledge gap by assessing the mobilisation and potential toxicity of dissolved metals under flow conditions induced by episodic high rainfall. Identifying key episodic rainfall-induced processes in the behaviour of pollutant metals can support future risk mitigation strategies in catchments.

4.2. Methods

This study focusses on the Hebden Beck catchment in northern England, where the underlying geology consists of a succession of sandstone and mudstone (Millstone Grit) and carboniferous limestone (Appendix 4.1). This headwater stream is affected by metal contamination derived from historical lead mining, where galena (PbS), sphalerite (ZnS) and barite ($BaSO_4$) were the profitable minerals. The catchment chemistry has previously been characterised (Valencia-Avellan et al., 2017) and assessed with respect to water quality and ecotoxicology under seasonal conditions (Valencia-Avellan et al., 2018). Three sampling stations were selected for this study: an ephemeral tributary (ET) located in the most upstream zone, draining an area of mine spoil wastes; a perennial tributary (PT) of an underground mine channel located in middle of the stream; and a site located downstream on the main channel (MC), 2.27 km from the River Wharfe confluence and adjacent to a flow gauging station (Appendix 4.2).

UK Meteorological Office daily rainfall data (UK Meteorological Office) were obtained for Pateley Bridge Ravens Nest (54°04'01.2"N 1°46'01.2"W) in order to present local seasonal drought and rainfall events for the month of August 2016 (> 12 mm during high rainfall days) (Appendix 4.3). The sampling campaign began at 1230h on 19 August and ended after a maximum of 96 hours at 1250h on 23 August 2016. Automated water samplers (Teledyne-ISCO, model 6712)

were set to collect at one or two hour intervals in each site. Automated samples were retrieved at the end of the sampling period (24-48 hours) and subsamples for each time interval were filtered in the field using syringe filters for metal and major ions (0.45 µm, polyethersulfone-hydrophillic, Sartorious) and for dissolved organic and inorganic carbon (0.45 µm nylon-polypropylene, Avonchem). Sample handling and *in situ* water quality measurements (pH, pH, SO_4^{2-}, DIC and DOC) followed previously used methods (Valencia-Avellan et al., 2017). Hourly rainfall data from Grimwith reservoir (code: 62046; 54°04'16.4"N 1°54'47.7"W; 3 km east of Hebden Beck) and flow data from a gauging station in the main river channel (code: F1960; 54°04'27.8"N 1°57'48.5"W) were obtained from the UK Environment Agency for the dates 18th to 23rd of August (Appendix 4.4). Several flow stages were identified; low-flow (LF), base-flow (BF), peak-flow (PF) and post peak-flow (PPF). Full details are in the Appendices section (Appendix 4.4). In ET, the first measurements were under stagnant conditions with the sampler positioned in a small pool near the confluence with the main channel. In PT and MC, data was collected from well-mixed areas with continuous flow. Metal analysis was conducted via ICP-MS (Thermo Fisher iCAPQc) using Certified Reference Material (SLRS-5) as a quality control and with specific limits of detection (Pb: 0.47 µg/l, Ba: 1.45 µg/l, Cd: 0.03 µg/l, Sr: 1.09 µg/l, As: 0.02 µg/l, Zn: 2.28 µg/l, Cu: 0.05 µg/l, Co: 0.014 µg/l, Ni: 0.06 µg/l, Fe: 1.43 µg/l, Mn: 0.15 µg/l, Al: 1.77 µg/l). In addition, two replicates per site and four field blanks were taken for procedural quality control. Activity of metals and solubility of relevant mineral phases were calculated using PHREEQC code (version 3) (Parkhurst and Appelo, 1999) and the WATEQ4F database (Ball and Nordstrom, 1991) where site-specific chemical data and major physico-chemical parameters were considered as input data. Changes in DOC concentrations during episodic events may influence the concentration of metal-organic complexes, therefore the Windermere Humic Aqueous Model (WHAM/Model VII) (Tipping et al., 2011) was applied to investigate chemical speciation of metals. Toxicity of metal mixtures including protons (H^+) and metals (Al^{3+}, Zn^{2+}, Pb^{2+} and Cu^{2+}) was estimated using WHAM-F_{TOX} (Stockdale et al., 2010). Procedures for WHAM/Model VII and

WHAM-F_{TOX} were followed the as described in Valencia-Avellan et al. (2018), detailed in Chapter 3.

4.3. Results and Discussion

The catchment hydrology responded rapidly to rainfall. Flow levels started to increase within two hours after the first period of rain (5 mm/h), indicating that runoff processes are likely occurring at the surface (overland flow) and subsurface (interflow) (Appendix 4.4). This rapid response has been reported when rainfall exceeds the infiltration capacity of the soil, especially in peat soils where the water infiltration is low (Holden and Burt, 2002).

Contrasting responses were identified for Pb and Zn under increasing flow conditions. Concentrations of Pb are directly influenced by flow variations showing a peak concentration (690.3 μg/l) corresponding with peak flow, principally in ET. Contrary to ET, a slow rise in concentrations was evident in PT with maximum values (211.7 μg/l) reached at post peak flow. This delayed response to episodic rainfall could be due to the subsurface runoff (interflow) percolating through mine channels (Seiler and Gat, 2007). High Pb concentrations in MC (153.7 μg/l) showed similar responses to ET but lower in magnitude (Figure 4.1a). Zinc concentrations showed an inverse relationship with episodic rainfall and flow variations (Figure 4.1b), although concentrations in ET showed mixed patterns. For instance, in ET at peak flow, concentrations immediately decreased (55%) but increased at post peak flow (194%). This can be associated with large masses of mine wastes exposed to water, producing abundant concentrations of dissolved Zn (Hudson-Edwards, 2003). Less marked dilutions (47% and 35%) and more stable concentrations were identified in sites PT and MC, perhaps due to discrete rainwater inflow in PT and MC having the lowest concentrations of the three sites. Maximum Zn concentrations were measured in ET (5016.8 μg/l), followed by lower concentrations in PT (1069.1 μg/l) and MC (693.6 μg/l). The observed trends suggest that episodic rainfall increases concentrations of dissolved Pb and has a lesser impact on Zn concentrations.

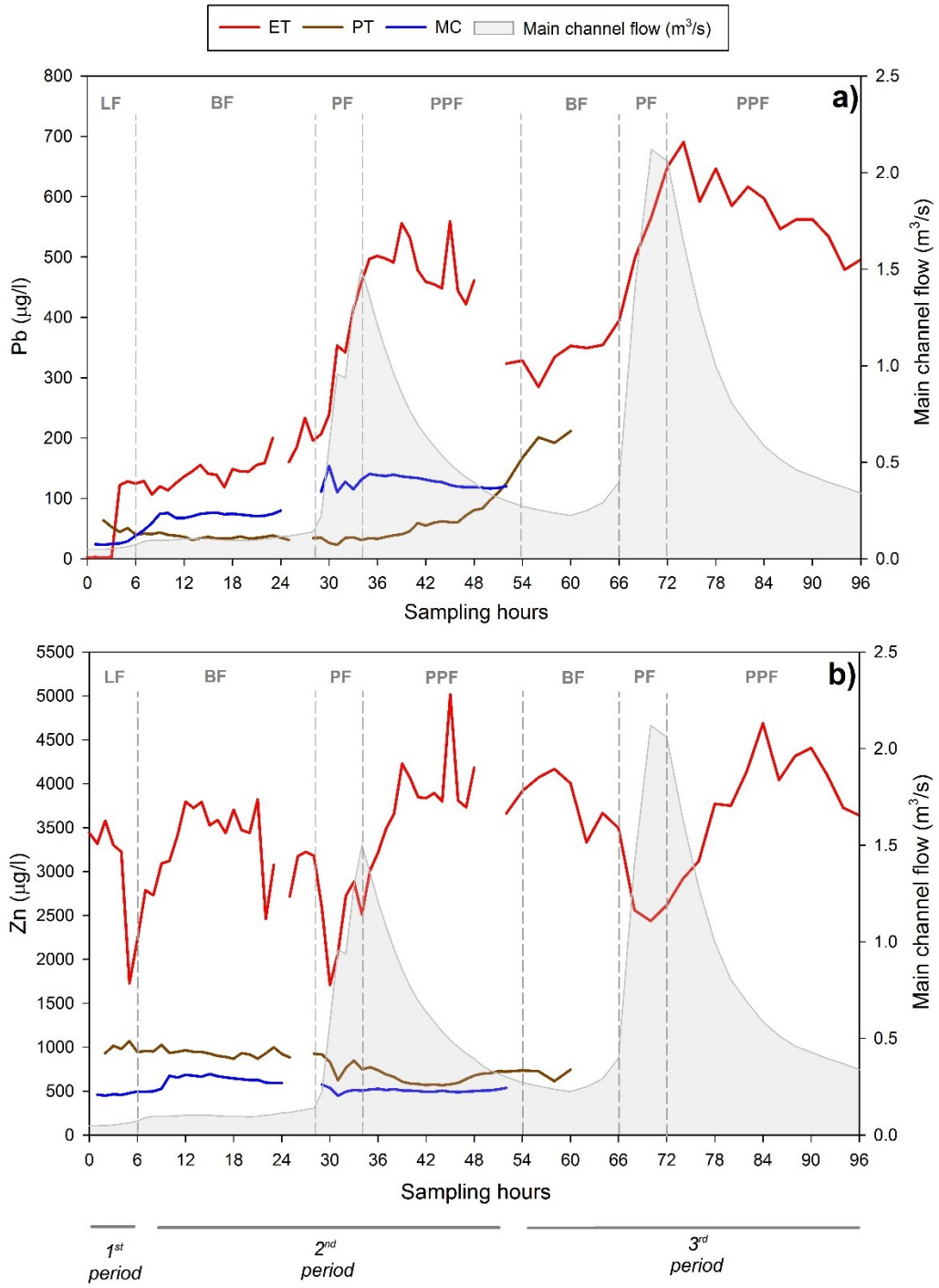

Figure 4. 1. Trends of metal concentrations (µg/l) at different sites during three rainfall periods. Panel a shows trends of Pb concentrations and Zn concentrations are indicated in panel b. The secondary Y axis shows flow data collected at the gauging station in main channel. Solid lines represent sampling sites and shaded area flow data. Perpendicular dotted lines indicate the flow stages at different rainfall periods.

Runoff has not altered the typical circumneutral conditions of the catchment. Thus, geochemical signatures of each tributary are controlling their major ion chemistries (e.g. SO_4^{2-}, DIC and DOC) (Appendix 4.5) (Jones et al., 2013;

Valencia-Avellan et al., 2017). Correlation analysis showed diverse relationships at different flow conditions. Generally, stronger positive correlations were present in ET between Pb and Zn with SO_4^{2-}, likewise in PT, where positive correlations were identified mainly between Zn with DIC and SO_4^{2-}, whereas in MC, Pb showed strong correlations with DOC (Appendix 4.6).

Runoff has an enhancing effect on weathering processes such as hydrolysis, oxidation and erosion. Geochemical processes under episodic rainfall are controlled by cerussite ($PbCO_3$) and smithsonite ($ZnCO_3$). Moreover, Pb is closer to saturation than Zn, with Pb activities close to saturation observed in ET and MC (Figure 4.2). This may be due to the slower kinetics of the smithsonite dissolution versus cerussite (Pokrovsky and Schott, 2002). These results agree with prior studies (Tame et al., 2017; Valencia-Avellan et al., 2017; Valencia-Avellan et al., 2018) and emphasize the importance of smithsonite and cerussite in controlling metal kinetics and transport (Hammarstrom and Smith, 2002).

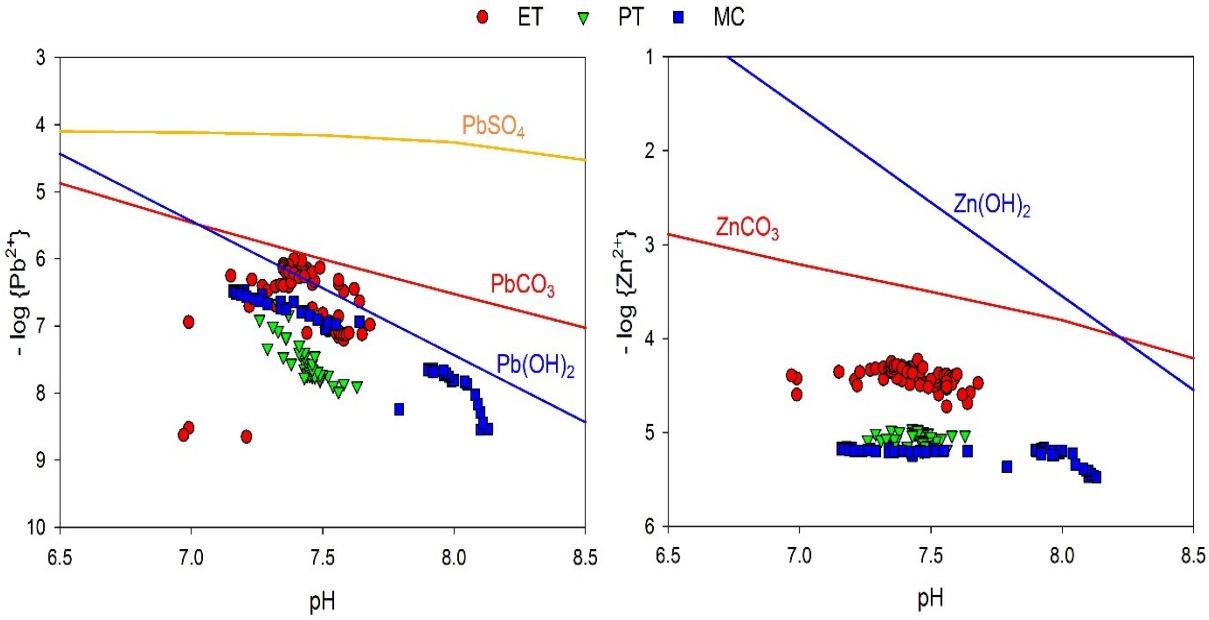

Figure 4. 2. Lead and Zn activity as a function of pH and site specific conditions of spoil wastes areas. Theoretical saturation of mineral forms represented by solid lines were obtained using pCO_2 = 0.0012 atm or by site specific averaging of SO_4^{2-} (ET: 13090 μg/l, PT: 10970 μg/l, MC: 6280 μg/l), Cl^- (ET: 3600 μg/l, PT: 5960 μg/l, MC: 5080 μg/l) and temperature (ET: 16.9 °C, PT: 9.5 °C, MC: 14.0 °C). The variability between sites was a maximum of 0.05, thus lines correspond to median values. The calculated activity of Zn from equilibrium with $ZnSO_4$ was > 1 mol/L. Note that the Y axis have different scale.

The ET data highlight the significance of extensive open spoil as a metal source during episodic flow (especially for Pb). An approximately linear increase occurred for Pb and Zn concentrations, but they are reduced at flow > 0.5 m^3/s (Figure 4.3). This suggests a bi-modal response of metals to flow, possible related to the exponential fall in DIC with flow (Appendix 4.7) influencing the saturation of the secondary minerals cerussite and smithsonite. Further evidence for this is given in Appendices, Appendix 4.8 and 4.9 as saturation index (SI) showed an immediate decrease when flow increases. Studies from Pokrovsky and Schott (2002) regarding geochemical processes under circumneutral conditions indicated that high flow may increase the concentrations of carbonate and bicarbonate ions, which act as inhibitors of smithsonite dissolution, reducing the equilibrium activity for Zn. Another research from Carroll et al. (1998) also mentioned the relevance of carbonate minerals in the sorption of metals as they function as long-term sinks, competing with other reactive minerals such as iron oxyhydroxides. Previous research in this catchment has identified that Pb is strongly associated with both particulate and colloidal forms, whereas Zn is

present mainly in inorganic complexes (Valencia-Avellan et al., 2017; Valencia-Avellan et al., 2018). Thus, during high flood periods the resuspension of sediments may increase the total concentrations of Pb (from particulate forms, and thus potentially available for the dissolved phase), whilst this will be a minor potential source of Zn (Elder, 1988; Nagorski et al., 2003).

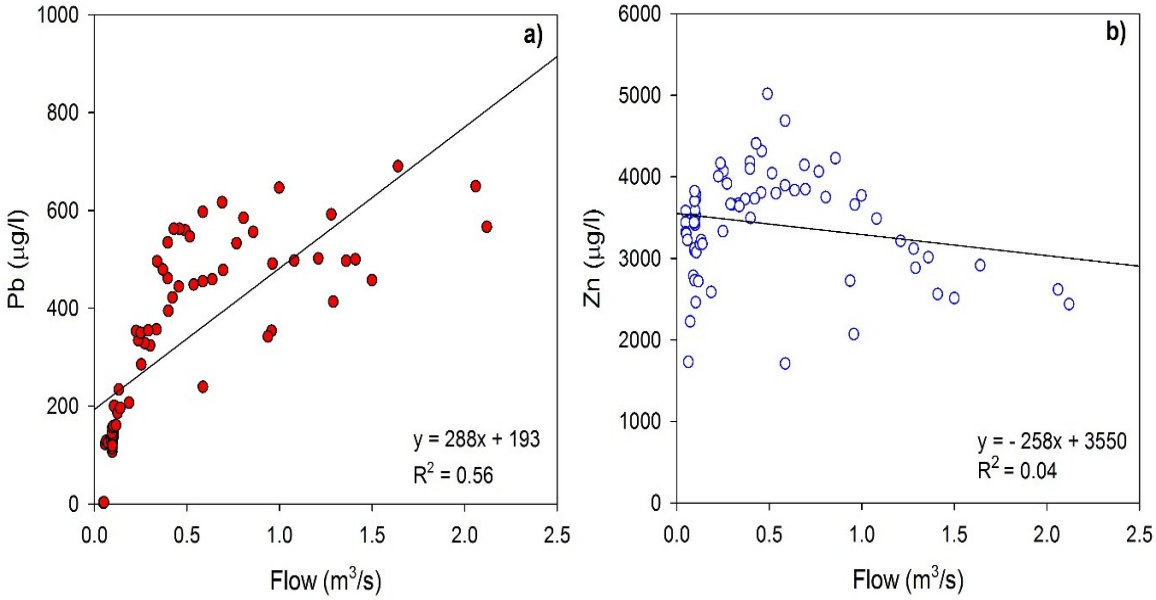

Figure 4. 3. Relationships between metal concentrations (µg/l) and flow across all three rainfall episodes in the ephemeral tributary. Note that Y axis have a different scale.

4.3.1. Effects of episodic rainfall on metal toxicity assessed using WHAM and WHAM-F_{TOX}

At all sites the highest concentrations of Pb-organic complexes and oxide bound Pb were calculated to occur at post peak flow. This could be explained by the increasing amounts of DOC, and concentrations of Fe and Al as precipitated minerals (e.g. hydroxides) at peak and post peak flow (Appendix 4.5). Nordstrom (1999) indicated that sorption of metals onto freshly precipitated Fe and Al hydroxides at circumneutral pH occurred as follows: Pb > Cu > Zn. This low affinity of Zn to surface sorption to oxide minerals was identified by the abundance of Zn-inorganic complexes (Figure 4.4). Moreover, estimations in the absence and presence of oxides precipitated similar concentrations resulted for Zn complexes (inorganic and organic), while Pb has a large tendency to be bound

to DOC and oxides principally in the presence of oxides precipitates (Appendix 4.10).

The impacts of climatic events on contaminant transport and water quality are complex because of localised effects. Current results are consistent with previous research on the transport and pollution of Pb occurring through particulate material, enhanced by episodic rainfall (Neal et al., 1997). Likewise Gozzard et al. (2011) reported the attenuation effect on Zn pollution during peak rainfall. Comparison of metal fluxes under episodic rainfall conditions revealed that local conditions such as the abundance of secondary mineral sources and circumneutral pH are key factors controlling the kinetics of Pb and Zn, whereas flow variations could be an enhancing factor. Thus, these results provide insight into other catchment where streams drain mine spoil under similar conditions.

The potential ecological risk of metal pulses was estimated using WHAM-F_{TOX}. We considered two conditions for calculating total toxicity values (Total_F_{TOX}): i) Total_$F_{TOX} \leq 2.33$, no toxic effects occur, and ii) Total_$F_{TOX} > 2.33$, toxicity reflects a risk of diminished macroinvertebrate species diversity, until no species are predicted to be present at a value of 5.20. Under flow conditions induced by episodic rainfall, toxicity function was calculated in ET showing values from 3-3.8 but not clearly related to flow induced metal concentration changes, lower toxicity values predicted in PT (≤ 2.1) and MC (≤ 1.7) suggest no toxic effects from dissolved metals (Appendices, 4.11, 4.12, 4.13). Overall, calculations during episodic flow showed that short term fluctuations in metal concentrations are not reflected in the predicted acute toxicity risk to aquatic organisms. This may be due to a number of factors including changes in concentrations of competing species, DOC and other ligands (Namieśnik and Rabajczyk, 2010). Future work would be better focused on sites with predicted ecological harmful levels of metal and perennial tributaries from spoil runoff areas, including a better understanding of variability during seasonal as well as episodic flow conditions.

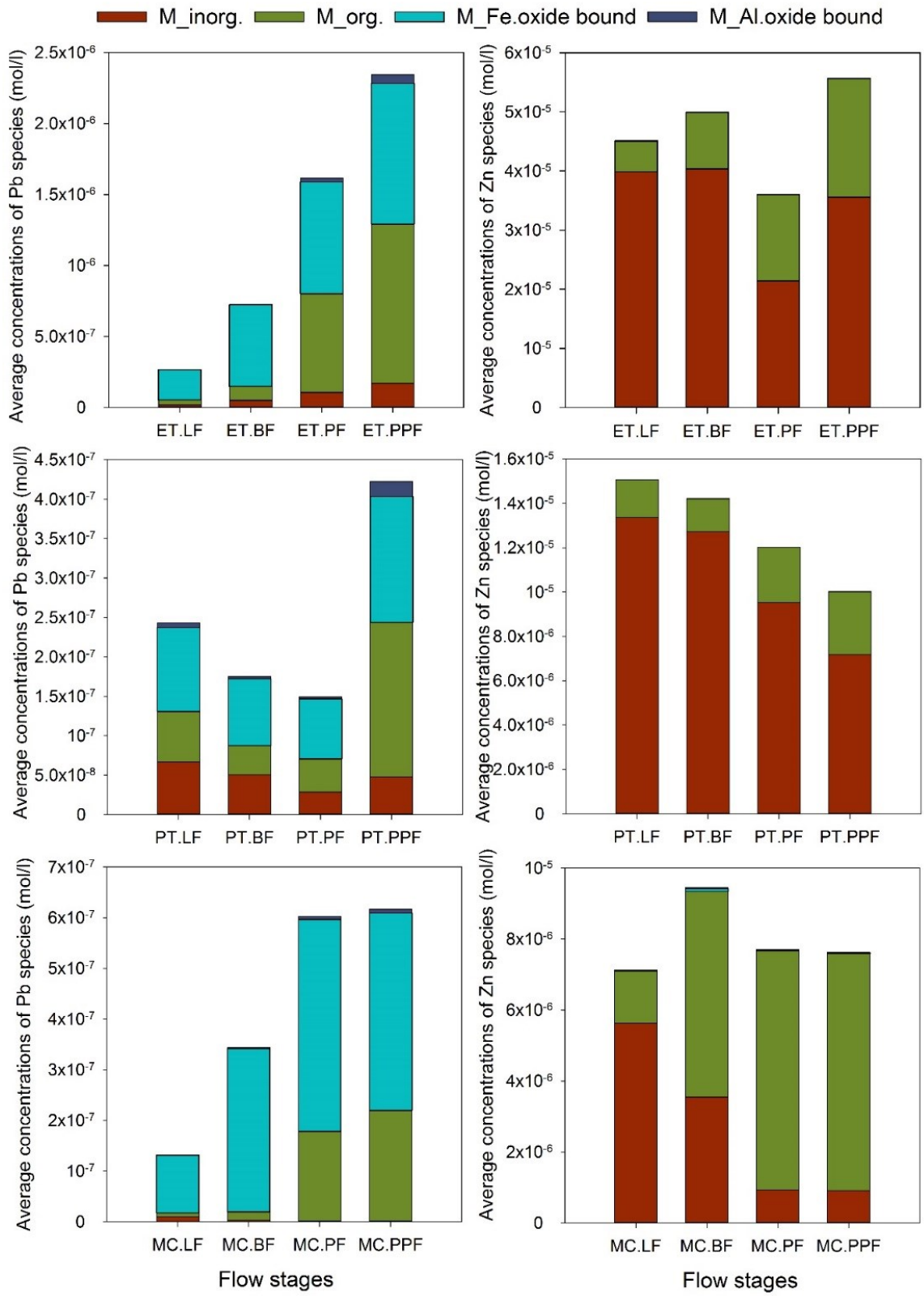

Figure 4. 4. Metal concentrations in presence of surface active oxide precipitates (Fe and Al oxides) calculated by WHAM/Model VII at different flow stages in all sampling sites. Left hand side panels show average concentrations of Pb. Right hand side panels show average concentrations of Zn species. Note Y axis have different scales.

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4.5. Conflict of Interest statement

The authors declare that there is no conflict of interest.

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Chapter 5: Public perceptions on water quality of a river affected by historical metal mining

Unpublished – In preparation

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Abstract

Policies within the European Water Framework Directive (EU-WFD) include the promotion of an integrated community policy on water. However, public participation and engagement initiatives included as part of River Basin Management Planning have been inadequate. To tackle this problem, policy-makers and decision-makers are encouraged to ensure effective transmission of new and existing technical knowledge through better communication with the public as part of a catchment-scale management approach. Thus, the present study focuses on the assessment of public perception (residents, visitors and stakeholders) of the water quality of a small upland river, within a protected area in northern England that is affected by heavy metal contamination from historical mining. Results show that mines are valued for their cultural legacy by residents, while visitors were more likely to show concerns related to the environmental legacy of mines. Awareness of water quality standards were starkly different between specialists and non-specialists, reflecting an insufficient transference of knowledge from technical to local community and potentially across stakeholders groups. Potential remediation strategies were more accepted by visitors than residents, but passive treatments were the preferred approaches to protect the village's landscape and surroundings. Awareness of the increasing frequency of

flood events was observed in residents and visitors, although a higher concern was observed for visitors, likely associated with individual experiences. Overall, results highlight the importance of the integrated involvement of specialist (environmental and government agencies), visitors and residents (e.g. villagers, farmers) for a holistic management of water resources and natural environments (e.g. rivers). In conclusion, a clear translation of scientific and technical knowledge to the public is essential for better understanding the environmental legacy of mines, in order to promote public awareness for improving the quality of this river ecosystem and protecting this conservation area.

5.1. Introduction

Freshwater systems provide countless benefits to the environment and human populations. The unceasing competition for water resources (e.g. domestic, industrial, and agricultural uses) have had a profound effect on many of these ecosystems. Furthermore, factors like climate change are having a direct or indirect impact in these water bodies, affecting adjacent populations. Sustainable development of these habitats is a difficult task for managers.

Nowadays, the management of freshwater needs to move from traditional approaches to more integrated initiatives. In the past, management policies have been primarily established by technical and scientific knowledge, leaving the role of the society underestimated (Flora, 2004). In the last half century, progress has been made in understanding freshwaters as integrated ecological systems. The inclusion of technical and social experts as productive partnerships have improved the management of natural resources, as engaged communities deliver greater ranges of perspectives for developing more effective policies (Tindale, 2014; Gain et al., 2013; Chirenje et al., 2013).

Policies within the European Union Water Framework Directive (EU-WFD) include the promotion of an integrated community policy on water. This is implemented by considering five key components: river basin districts, river basin management planning, public participation, economic analysis, and policy integration. In England and Wales, pollution from diffuse sources is a long-term problem for water bodies due to mine drainage, for example in northern England

over 12000 km^2 of catchments have been affected by historical mining (Howard et al., 2015; Macklin et al., 1997). Thus, for compliance with the WFD, the River Basin Management Planning included public participation and engagement initiatives, although implementation was inadequate (DEFRA, 2013). In 2017, a survey on the current opinion of water management and community engagement initiatives in the UK and the Republic of Ireland indicated that more than 80% of respondents did not feel included in decisions about their water environment (Rolston et al., 2017). Thus, a new catchment-scale management or catchment based approach (CaBa) encourages policy-makers and decision-makers to ensure the effective transmission of new and existing technical knowledge through a better communication with the public (Voulvoulis et al., 2017).

In understanding people's general knowledge, awareness, and beliefs about water, discovering agreement as well as differing perspectives is the first step for creating an effective place-based assessment (Hu, 2011). This information can provide a foundation for negotiating differences and building common ground that can motivate cooperative environmental planning to improve water quality (European Commission, 2003). Thus, the present study focuses on the public perception of a small upland river part of the Upper Wharfe catchment, Hebden Beck, located in North Yorkshire, UK. This river has been affected by heavy metal contamination from the lead mine industry (leading to exceedances of water quality standards set by the WFD and implemented in England and Wales by the Environment Agency), as well as by flood events (Jones et al., 2013; Valencia-Avellan et al., 2017). This study aims to identify public awareness of river ecosystem services, perceptions of river water quality, opinions about flood effects and response to potential metal remediation practices.

5.2. Methods

5.2.1. Study area

The research was undertaken in the parishes of Hebden and Grassington from the Craven District of North Yorkshire, UK. Both villages are part of the Yorkshire Dales National Park. The study was focused in Hebden, located at an altitude of 190 meters (above sea level) on the north side of Wharfedale. It sits adjacent to

the steep sided valley associated with the fast flowing Hebden Beck, about 3 km from its source on Grassington Moor and approximately 750 meters from its confluence with the River Wharfe (south). The village's location is strongly influenced by local geography. It sits across an important bridging point, as the valley of Hebden Beck narrows slightly at a contour height which is convenient for east to west communication.

In 1791, cotton production began in Hebden with the construction of a large cotton mill, becoming a major industry for the village. New steam powered machines dominated the rural water powered mills, ceasing the production in 1870. During the late 18th and early 19th centuries, lead mining became a major industrial activity, although this probably remained as small-scale enterprise in Hebden. In 1856, the Hebden Moor Mining Company was formed but the extraction only continued for 17 years, causing a dramatic effect on the character of the village. Hebden is important in terms of its architectural and historic interest. Therefore, on 28th March 2006 the village and its surroundings were designated as a conservation area by the Yorkshire Dales National Park Authority (Yorkshire Dales National Park, 2006).

Hebden's orefield comprised coal and lead-zinc mineral deposits, where galena is the most common mineral, sphalerite, chalcopyrite, barite, fluorite, calcite and witherite are also relevant minerals. Early mining involved the erosive power of water to uncover mineral veins, water power was used in dressing floors and smelt mills, producing large amounts of mine wastes in close proximity to the river, Hebden Beck (Gill, 1993).

5.2.2. Survey strategy and data analysis

Three groups of respondents were identified: residents, tourists and stakeholders. The resident's survey was performed only in Hebden. The survey was conducted through completion of a questionnaire designed to capture semi-quantitative responses. The survey methodology involved an *in situ* questionnaire for residents and visitors and an online survey to stakeholders (Table 5.1). Questionnaires were prepared using slightly different wording to capture similar information and compare perceptions between groups. The questionnaires were

divided in four sections: i) awareness of river ecosystem services, ii) perception of river water quality and roles of regulators, iii) effects of the mines and flood events on river water quality, and iv) socio-demographic information. In addition, an information sheet about the purpose of the survey was included.

Table 5. 1. Applied surveys and specific approaches.

Type of survey	Specific approaches	Additional information
Resident's survey (July-August, 2016)	Survey was performed only in the village of Hebden. Census data (Office for National Statistics-UK) was used for estimating the population size. The questioner knocked on every household door, one person was questioned for each household. In case of no response, the survey was placed in the mail box with a notification indicating the next collection date and the availability of the online version.	Ethical approval (Appendix 5.1) Resident's questionnaire template (Appendix 5.2)
Visitor's survey (July-August, 2016)	In parallel with resident's survey. Public areas like walking paths near Hebden Beck and the river Wharfe, were used as sampling points. In addition, village business (e.g. pub and tea room) were considered for distributing flyers and publicising the online version.	Visitor's questionnaire template (Appendix 5.3)
Stakeholder's surve(April-June, 2017)	A list of stakeholders was prepared. An invitation email was sent to 30 organizations associated with the National park authority, environmental protection, water management agencies, river organisations, cultural heritage groups, mining societies, associations for protection of biodiversity and wildlife, and tourism companies. Survey was online from 11-04-2017 to 02-06-2017.	Ethical approval (Appendix 5.4) Questionnaire template (Appendix 5.5)

The obtained qualitative data were scored and transformed to numerical data (Appendix, 5.6). Descriptive statistical tests were performed to obtain frequencies and percentages (Appendix 5.7). Responses from a semi-structured interview carried out in July 2016 to a local historian were used as complementary information for this study.

5.3. Results

5.3.1. Public perceptions of Hebden Beck as provider of environmental and business services.

Environmental amenities like wildlife habitat, attractive focus to the village and source of drinking water were associated with the importance of Hebden Beck

(Figure 5.1). For residents, the first two amenities had a significant value for residents (67% and 51%) as well as for visitors (65% and 53%). High scores for "provision of wildlife habitat" is likely because, as part of a National Park, Hebden Beck supports key environments of international importance such as limestone pavements, limestone grasslands, blanket bog, upland heath and upland hay meadows, and this will be the reason people visit the area. In addition, Hebden Beck as an attractive focus for the village was highly rated since it provides a strong sense of tranquillity and remoteness. Despite some visible scarring of the landscape related mainly to mining, this river provides many opportunities for outdoor recreation activities like walking and cycling, where information boards are displayed (e.g. interpretation panels) to enhance understanding and appreciation of mines as sites with historic significance, therefore considered scheduled monuments (Yorkshire Dales National Park, 2006; White, 1998).

Regarding the role of the river as source of drinking water, opinions varied reflecting the incomplete knowledge about Hebden Beck in this context. This misconception possibly happened because residents experienced a severe period of drought during the 60s and 90s, and water authorities used a groundwater tributary from mines (e.g. Duke's level) as a temporary source for drinking water (Lakin, 1999).

In addition, opinions about business amenities derived from the presence of the riverine ecosystem were evaluated (Figure 5.2). Responses reflect that farming and fisheries are considered by residents as the most important activities (61%) for the local economy, followed by the attraction of visitors to the village-tourism (23%). This preference is likely associated to the fact that farming has been the main and oldest economic activity in Hebden. Conversely, visitors perceived tourism as the most important commercial activity (58%), while farming and fisheries were considered as the second more relevant (38%). The recognition of visitors as important business in the village, shows an opportunity to involve them in supporting conservation efforts in Hebden.

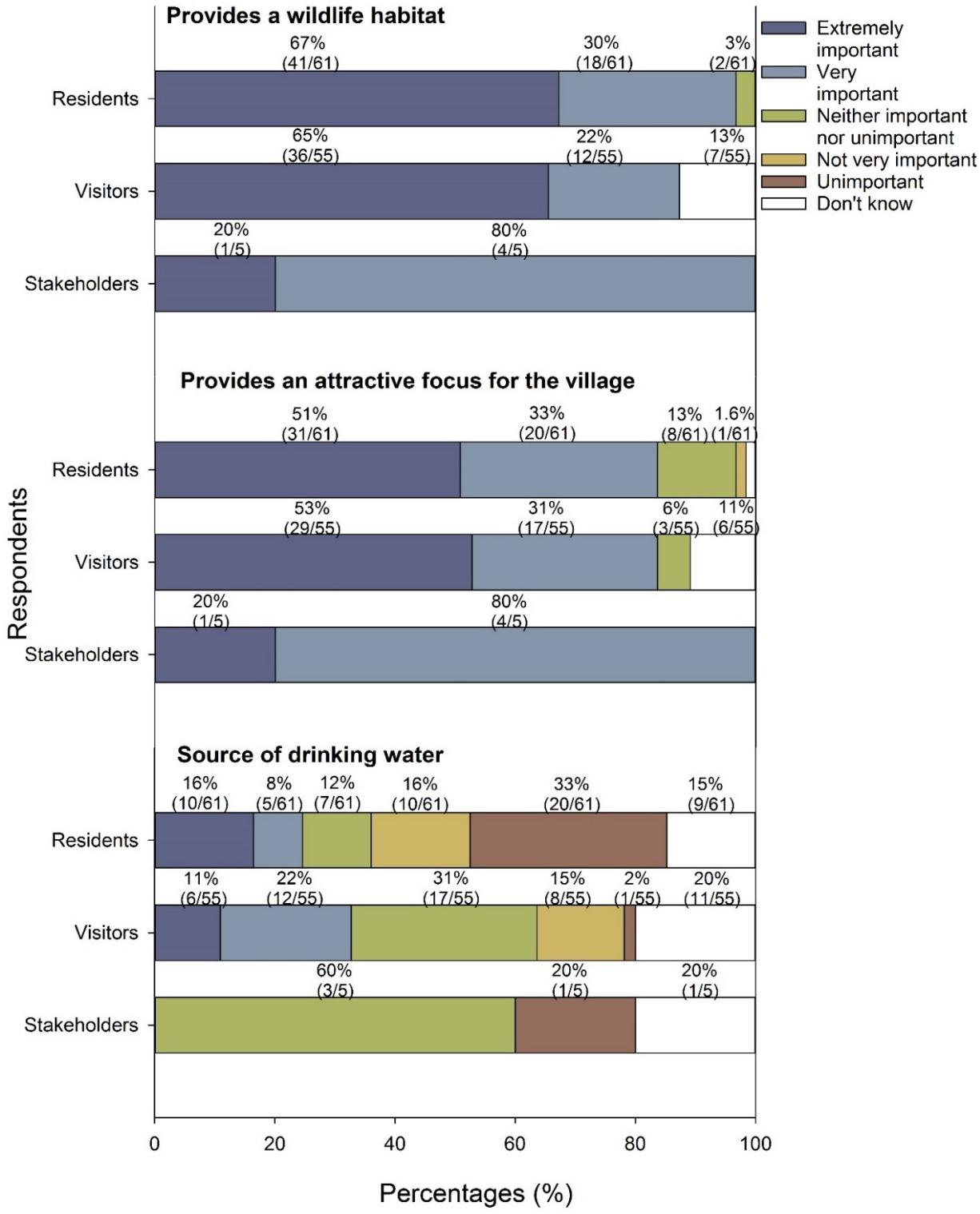

Figure 5. 1. Opinions about the importance of Hebden Beck in providing environmental services in the village.

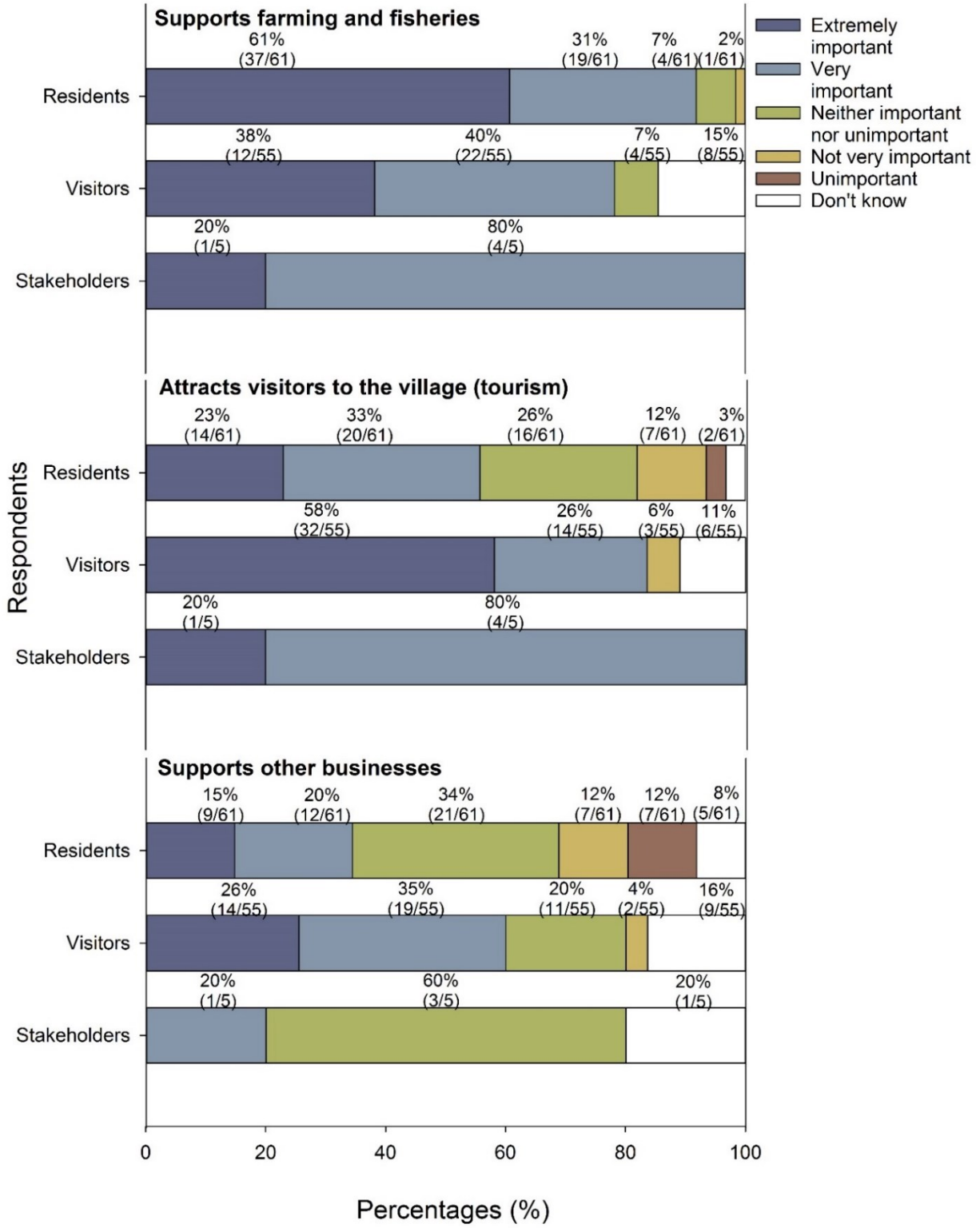

Figure 5. 2. Opinions regarding the relevance of Hebden Beck in supporting business services in the village.

5.3.2. Respondent's awareness of river water quality.

In the UK, the Environment Agency is responsible for assessing the water quality of all water bodies. In this section, respondent's awareness about the organisation in charge of the quality of Hebden Beck was assessed. Results showed that about 47% of residents and 44% of visitors recognised the Environment Agency as the responsible authority, although for more than 50% different responses were given (Table 5.2). Likewise, awareness of national quality standards for rivers was also assessed. Table 5.3 shows that all groups were acquainted with the standards, but levels of awareness were higher for stakeholders (80%), followed by residents (54%) and visitors (42%). Additionally, respondents were asked for their opinion regarding the overall status of the water quality of Hebden Beck. Figure 5.3 shows more than 50% of residents and visitors rated the river water within the criteria "High" and "Good", while 40% of stakeholder's rates were "Bad". When clustering the responses as groups of non-specialists (e.g. residents and visitors) and specialists (e.g. stakeholders), results suggest that non-specialists considered mostly field observations like colour or odour, whereas stakeholders solely expressed their technical knowledge outlining the actual status of the river, or not giving an opinion where the facts were not known (Figure 5.3). These responses reflect that water-related problems (e.g. pollution) are distanced from public debate and generally defined as technical matters to be known and handled by experts in specialised agencies (Batterbee et al., 2012).

Table 5. 2. Knowledge about responsible organisation for assessing water quality of Hebden Beck.

Organisations	Residents	Visitors
Yorkshire Water	29% (18/61)	22% (12/55)
Environment Agency	47% (29/61)	44% (24/55)
National Park Authority	-	7% (4/55)
Yorkshire Water/ Environment Agency	-	11% (6/55)
Yorkshire Water/ National Park Authority	-	4% (2/55)
Other. Please state	7% (4/61)	-
Don't know	16% (10/61)	13% (7/55)

Table 5. 3. Awareness of national quality standards for rivers.

	Residents	Visitors	Stakeholders
Yes	54% (33/61)	42% (23/55)	80% (4/5)
No	34% (21/61)	47% (26/55)	20% (1/5)
Don't know	11% (7/61)	11% (6/55)	-

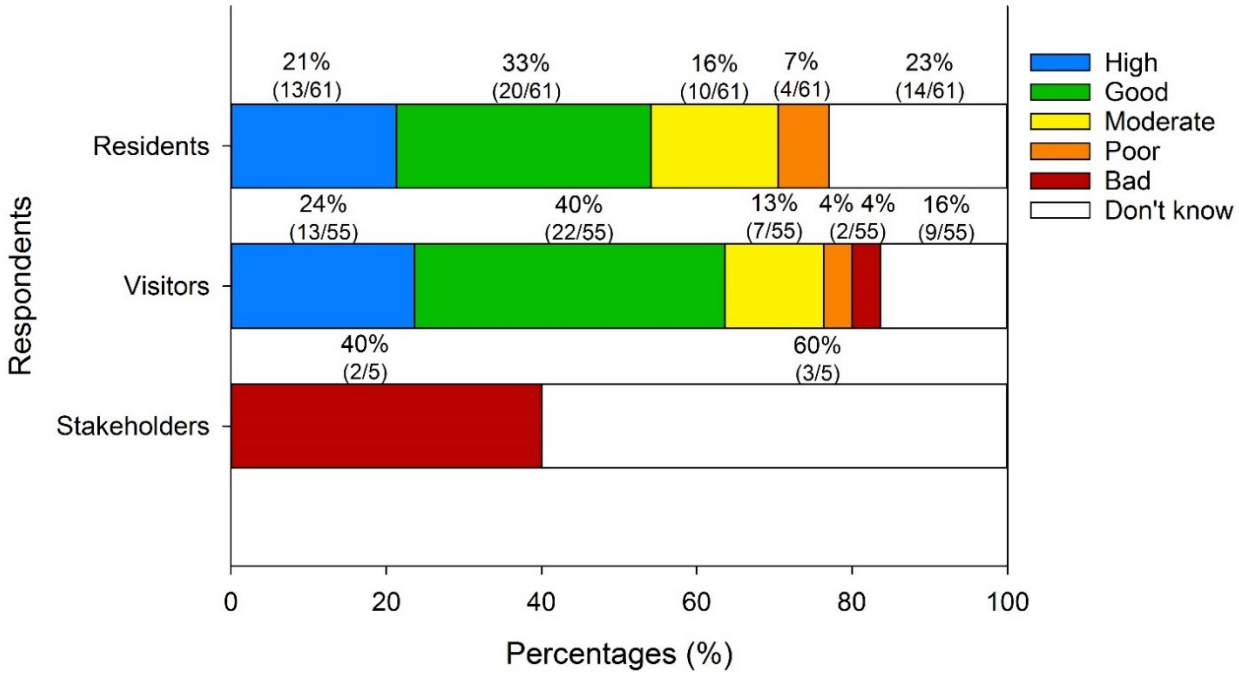

Figure 5. 3. Public perceptions about Hebden Beck's water quality. Criteria were matched with categories established by the Water Framework Directive (UK-TAG, 2007).

Table 5.4 demonstrates opinions from residents and visitors regarding the improvement of Hebden Beck's water quality. Despite that more than 60% of visitors considered the river's status either high or good quality (Figure 5.3), this group had a more flexible attitude than residents in relation to potential improvements of the quality of the river using remediation technology. This is probably because some visitors (e.g. fly fishers) have a better understanding of river quality.

Table 5. 4. Opinions about the improvement of water quality from Hebden Beck.

Responses	Residents	Visitors
Yes	15% (9/61)	29% (16/55)
No	36% (22/61)	27% (15/55)
Don't know	49% (30/61)	44% (15/55)

5.3.3. Mining in Hebden: cultural and environmental legacy

This section provides the perception of residents and visitors regarding the cultural and environmental legacy of mining. Results indicate that about 92% of residents consider the mines an important part of their cultural legacy. In the case of visitors, 55% agreed that the mines form an important part of the areas cultural legacy, whereas around 45% knew little or nothing about mines in Hebden (Figure 5.4). Nevertheless, both groups agreed that the mines had historic and present effects on water quality as shown in Figure 5.5.

The awareness of metal pollution was assessed based on previous studies reporting the significant impact of mining in Hebden Beck (Barber, 2014; Jones et al., 2013; Valencia-Avellan et al., 2017; Valencia-Avellan et al., 2018). For a better comparison, four statements about possible impacts of mines in the river water quality and farming activities were provided. Outcomes showed that greater awareness was generally reflected by visitors than residents (Figure 5.6). The disagreement of residents about the effect of mines in farming activities were unexpected, because since farmers (e.g. fish farmers, sheep farmers) was included in the resident's group a greater awareness might have been expected. However, it is possible that farming community was not adequately represented within resident's group. Contrary to residents, visitors showed more awareness of the latent effects of mines in farming activities. However, significant percentages of uncertainty (≥44%) were provided by both groups in topics regarding discharge of metals into the river and the effects of heavy rainfall in increasing metal pollution.

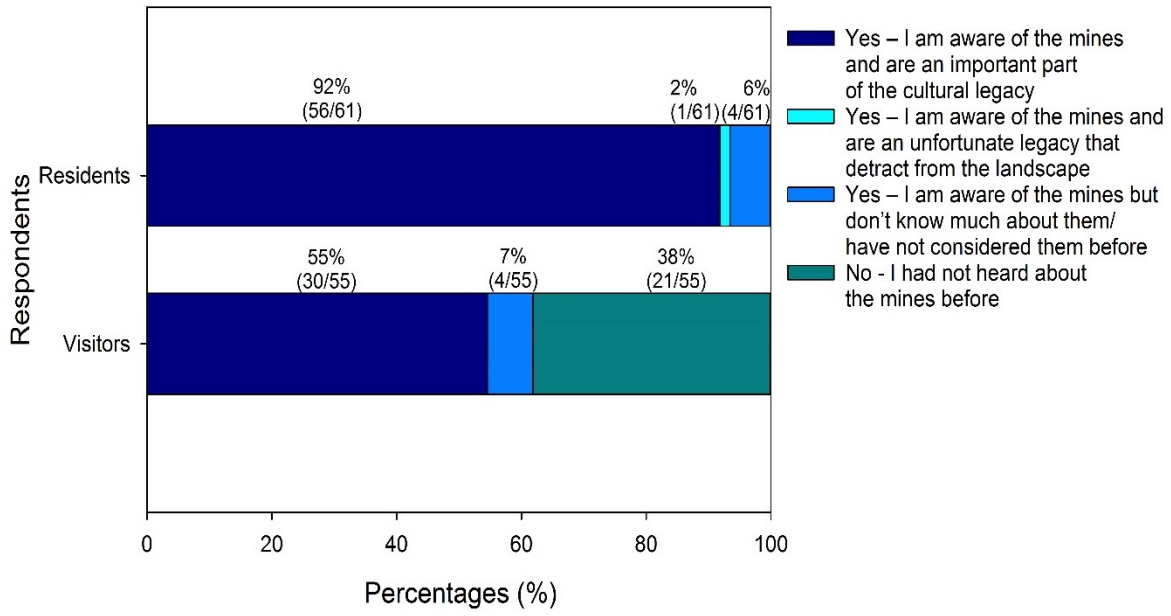

Figure 5. 4. Perception of the cultural legacy of mining in Hebden Beck.

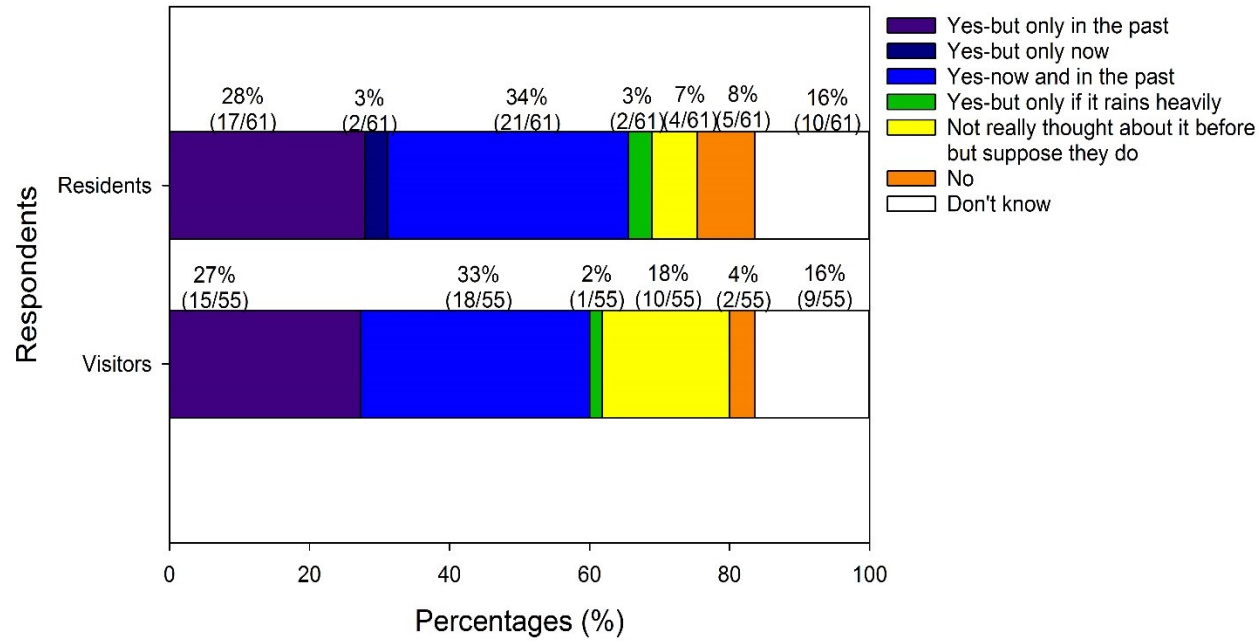

Figure 5. 5. Perceptions of the environmental legacy of mining, focused in Hebden Beck's water quality.

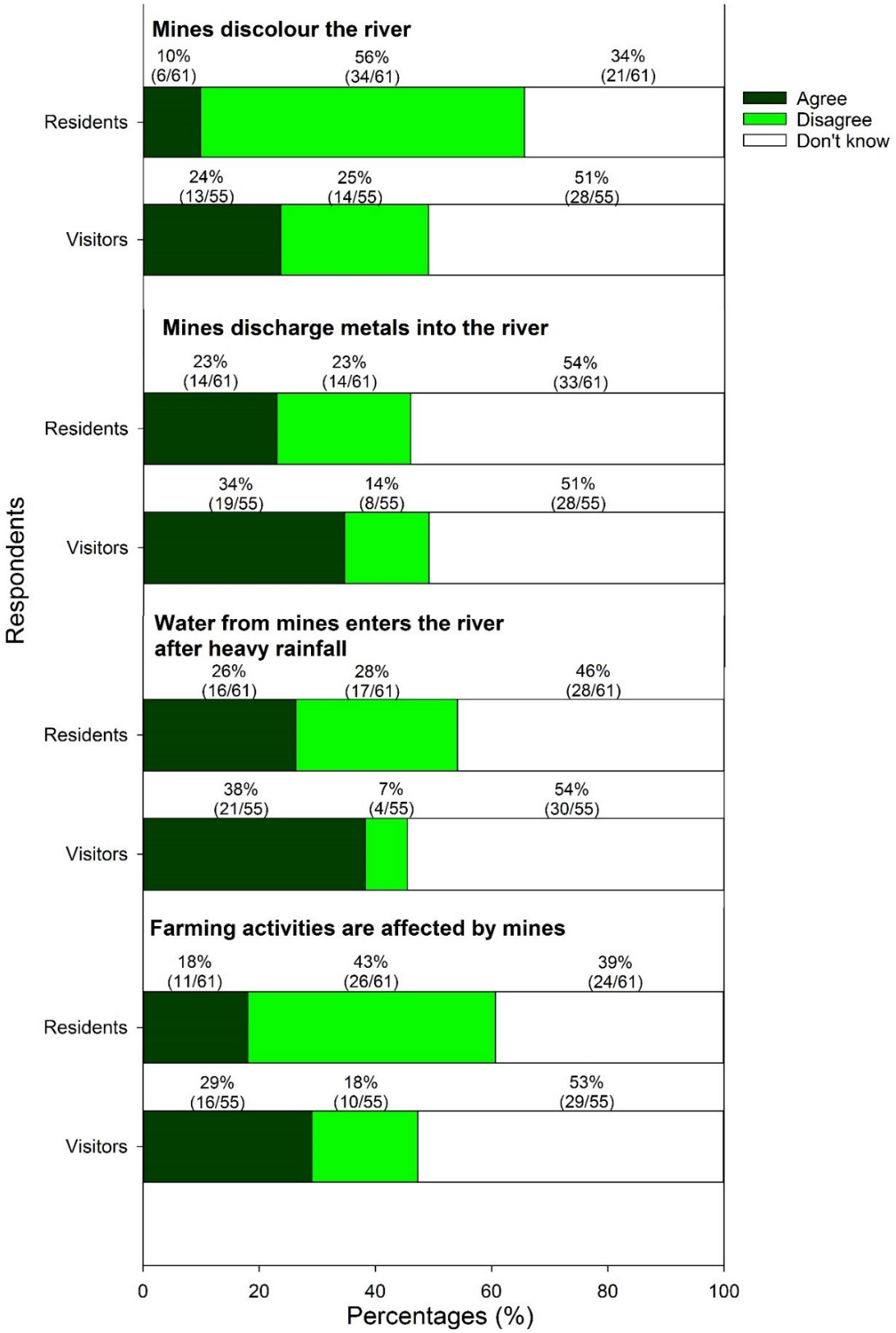

Figure 5. 6. Public awareness about mines as sources of metal pollution.

It can be inferred that residents have primarily known mining for the cultural rather than its environmental legacy. A reason could be that mining had a visible impact in the development of the village (e.g. cultural, economic). Likewise due to the national importance of mining infrastructure, mines have been acknowledged as Scheduled Monuments (White, 1998). Whilst environmental legacy of mining tends to be a passive impact, metals are underestimated in river water as signs of pollution are not observable. Greater environmental awareness from visitors might be related to some knowledge about presence of mines and their archaeological and historical importance for Hebden, as shown in Figure 5.4 and Appendix 5.8.

5.3.4. Perceptions of flood

Figure 5.7 shows that 20% of residents and visitors have been directly affected by flooding. Although both groups showed a great awareness to the increasing frequency of these events, possibly associated with recent national flood events (e.g. December 2015). Particularly, Figure 5.8 reveals a higher concern from visitors, indicating that environmental perceptions of flood are likely related to respondent's physical surroundings and experiences.

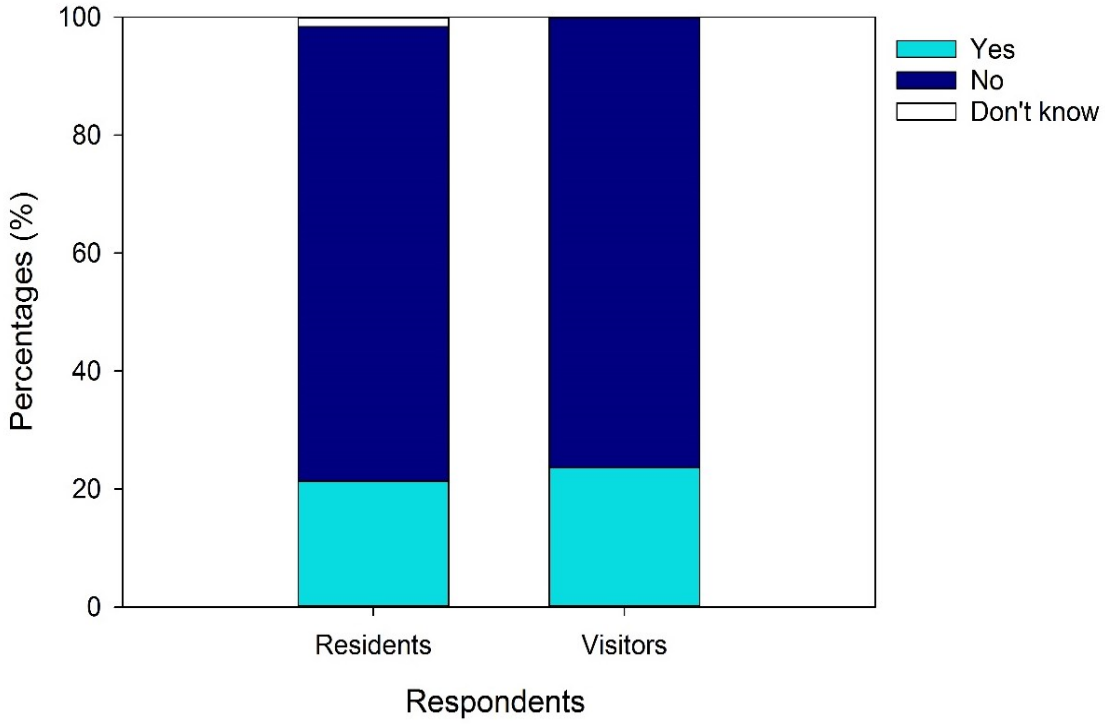

Figure 5. 7. Percentage of respondents affected by flooding.

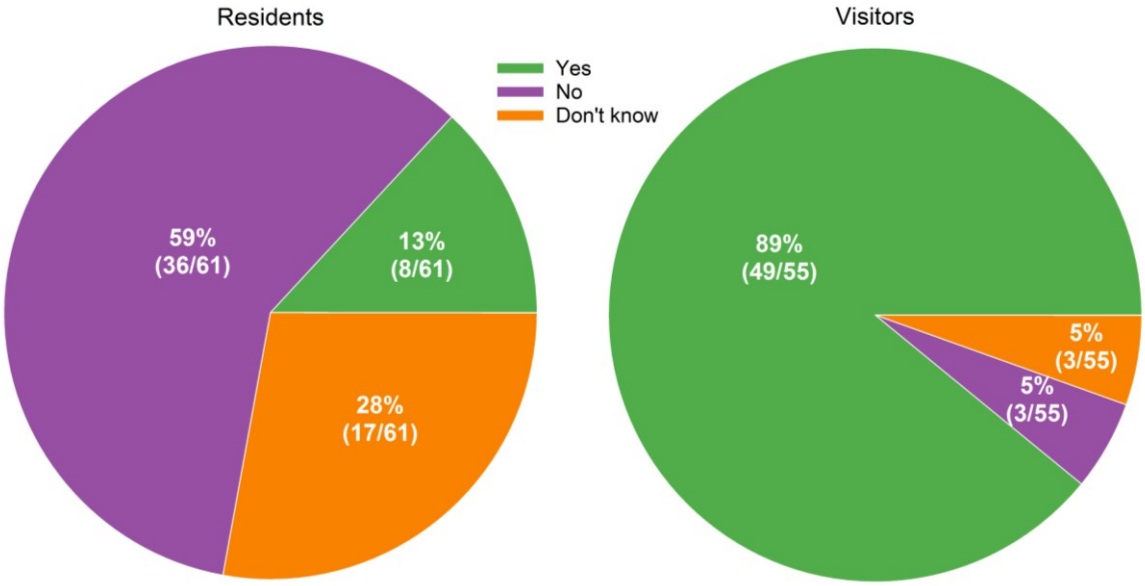

Figure 5. 8. Percentages about the awareness of respondents to increasing river water levels.

5.3.5. Opinions regarding metal remediation technologies

The disposition of residents and visitors to remediation or treatment technologies was evaluated (Table 5.5). Results indicate that most of the residents were unsure about remediation actions, probably because they have either greater concern of the visual impact of remediation or a perception that the problem is not serious enough to warrant remediation, or a combination of the two. Visitors supported the idea of limestone ponds and artificial wetlands, demonstrating their concern about water quality and their preference for passive approaches to protect the harmony of the surroundings. These choices are likely correlated with the high scores given to landscape and wildlife, and walking and leisure pursuits as the most important attractions in Hebden (Appendix 5.8 and 5.9).

Table 5. 5. Opinions of respondents about metal remediation strategies.

Remediation/treatment	Residents	Visitors
Creation of artificial wetlands	16% (10/61)	16% (9/55)
Creation of limestone ponds	2% (1/61)	35% (19/55)
None of the above - continue as is now	21% (13/61)	13% (7/55)
Don't know	25% (15/61)	13% (7/55)
Creation of artificial wetlands/ Creation of limestone ponds	16% (10/61)	16% (9/55)
Creation of artificial wetlands/ Use of water treatment plant	5% (3/61)	-
Creation of artificial wetlands, Don’t know	2% (1/61)	-
Creation of artificial wetlands/ Creation of limestone ponds/ Use of water treatment plant	13% (8/61)	7% (4/55)

Generally, the preferred remediation options were the creation of artificial wetlands and limestone ponds, thus with any future remediation efforts in Hebden Beck, these passive treatments should be considered the preferred options. Baxter (2015) carried out a research about small-scale remediation technologies in Hebden Beck, suggesting the deployment of passive filter media such as hydrous ferrous oxide (HFO). Based on these two outcomes, an agenda for Hebden beyond mine preservation could be proposed where scientists, environmental managers, local business, heritage specialists and general public (residents, visitors) consider strategies for river pollution mitigation and landscape protection (Howard et al., 2015).

5.3.6. Public engagement for Hebden Beck's management

The stakeholder group were asked their opinions about public engagement. About 60% of respondents agreed that greater public awareness in Hebden would be beneficial. Most of them were aware of the benefits of public engagement, as an opportunity for sharing different community needs associated with the river to reach consensus decisions.

For a representative assessment of the interaction of regulatory agencies with community members from Hebden, responses to a semi-structured interview from a local historian were appraised. The respondent was asked about the local awareness of Environment Agency monitoring in Hebden Beck, and the following comments were given:

"I think people are aware of everything [the EA is doing]. But providing it [the monitoring and assessment] doesn't mean that you are involving them [residents] directly, well they [residents] would say, it's happening, it's not to do with us".

"As a local historian. I would be [interested in the EA findings]. Because now it [the EA data, has] just disappeared into a black hole as far I'm concerned. It will be nice to have a summary about what they are finding and why they are doing it. As similar with the parish council, presenting something not in a weekly or monthly basis just once a year about what they are finding and how trends are changing. That would be very good".

"I don't think the Environment Agency is deliberately being secretive. They are just getting on with their job but not considering that what they are doing will have a local interest".

In addition, opinions about pollution solutions involving managing the spoils were also explored.

"I think some of the buildings are historical hugely important (e.g. Bolton Gill level, Duke's level). But spoil heaps are heaps to spoil".

The transcript of the whole interview is in Appendix 5.10.

Stakeholders provided more ideas for improving the public engagement in Hebden Beck. For instance, the application of good practices developed by some Rivers Trust as part of catchment partnership and the involvement of all interested parties (e.g. residents, landowners, local council, Coal Authority, Environment Agency, National Park Archaeologists and English Heritage) to

come up with well-meaning proposals to deal with water quality issues. From these opinions, the pollution management dilemma caused by the cultural and historical context of mines and their structures in Hebden could be better managed with the participation of all the interested groups. This study gives a snapshot of potential benefits of supporting a more integrated participation for an effective catchment management.

5.3.7. Demographic information

People were very cooperative with few of those asked unwilling to take part. A high response rate was observed for residents, followed by visitors and stakeholders (Table 5.6).

Table 5. 6. Response rate of the surveyed groups.

Groups of respondents	Number of prepared surveys	Number of refusals	Number of completed surveys	Response rate (%)
Residents	120	4	61	51
Visitors	120	6	55	(*)
Stakeholders	30	0	5	20
TOTAL	230	10	121	51

(*) *It cannot be calculated as the sample size was unknown. Refusals were recorded only from those approached.*

The nature of the respondents was examined with respect to their socio-demographic characteristics. A range of social descriptors (age, gender and employment status) were examined for residents and visitors (Table 5.7 and 5.8) (Figure 5.9). Residents and tourists showed age ranges mainly from 44 to >70 years old, although residents showed a greater percentage in the range 44-56. The largest demographic of the respondents was male and retired.

Table 5. 7. Percentages of age ranges from residents and visitors.

Age Range	Residents	Visitors
18 - 30	5% (3/61)	5% (3/55)
31 - 43	2% (1/61)	5% (3/55)
44 - 56	34% (21/61)	29% (16/55)
57 - 69	28% (17/61)	29% (16/55)
>70	28% (17/61)	31% (17/55)
Other	3% (2/61)	-

Table 5. 8. Gender of residents and visitors.

Gender	Residents	Visitors
Male	43% (26/61)	51% (28/55)
Female	34% (21/61)	42% (23/55)
Other	23% (14/61)	7% (4/55)

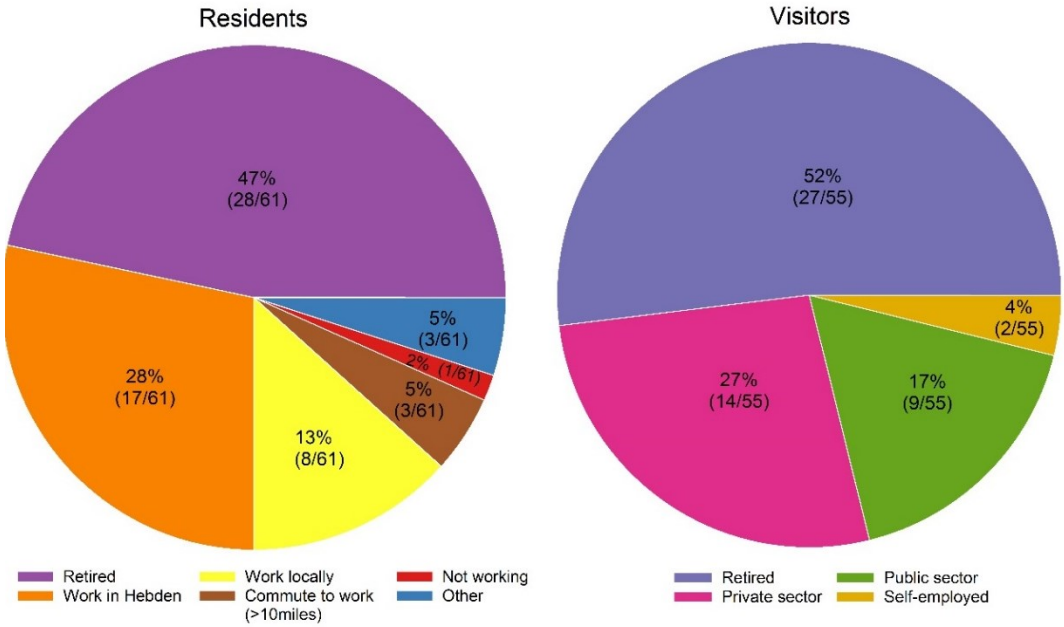

Figure 5. 9. The employment status of residents and visitors.

5.4. Conclusions

- Hebden Beck supports key environments of international importance such as limestone pavements, limestone grasslands, blanket bog, upland heath and upland hay meadows. It also contributes with farming and fisheries activities, therefore, Hebden Beck is very important for residents, visitors and stakeholders.
- Different perceptions on water quality from specialist and non-specialist showed an inadequate transference of knowledge from technical to local community and potentially across stakeholders groups.
- Hebden Beck water quality's perceptions from non-specialist (residents and visitors) are based on field observations (e.g. colour or odour).
- Mines are for residents an important cultural legacy, while for visitors they are more likely to be considered latent pollutants to the riverine ecosystem.
- Residents and visitors showed a lack of understanding about the influence of mines in metal pollution, compared to the findings of prior studies by this author and the Environment Agency.
- Awareness was identified for the non-specialist group about increasing frequency of river water levels.
- Remediation strategies were more acceptable for visitors than residents, both groups preferred approaches that protect the landscape of the village and its surroundings.

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Chapter 6: Synthesis and conclusions

6.1. Research Synthesis

Historical metal ore mining has produced severe damage to riverine ecosystems worldwide. Water discharged from mines is considered a major cause of metal pollution in many catchments, affecting water and sediment quality (Dennis et al., 2003; Byrne et al., 2012). Compliance with water quality standards is problematic due in part to the high levels of pollution produced from many point and diffuse sources but also because local environmental conditions influence metal fate and behaviour (Allen and Hansen, 1996; Hering et al., 2010; Valencia-Avellan et al., 2017; Valencia-Avellan et al., 2018). In the last few decades a variety of *in situ* analytical approaches and models have been developed to improve knowledge about the dynamic processes of metals in natural waters (Buffle, 2000; Kalis et al., 2006; Tipping et al., 2011). However, a variety of factors make the assessment of metal pollution problems a real challenge (Merrington, 2016), those include:

- Low concentrations of metal mixtures;
- Dynamics of metals in response to water chemistry conditions;
- Certain form of metals influencing bioavailability and toxicity to aquatic biota;
- The importance of some metals as essential for the functioning of biological processes;
- Increasing anthropogenic sources with temporal and spatial variations.

More research and monitoring programmes are needed to understand metal ion speciation, mobility, accumulation and bioavailability in river systems. This thesis investigated heavy metal contamination from a small catchment (Hebden Beck) affected by historical mining in the northern Pennines Region of North Yorkshire, UK. A variety of heavy metals (zinc, lead and cadmium) associated with sphalerite and galena extraction and processing have been detected in soil, stream and groundwater, causing deterioration of water quality in the catchment (Jones et al., 2013; Valencia-Avellan et al., 2017). The main aims were to assess the sources, mobility and toxicity of metal pollution in Hebden Beck and to

evaluate the public perception of mining impacts in riverine ecosystems for better management of contaminated rivers and improving water quality status.

Results presented in this thesis show that high metal concentrations are associated with oxidation of sulphide minerals (e.g. sphalerite and galena) and secondary minerals like metal carbonates (smithsonite and cerussite), producing neutral mine drainage. These findings agree with previous assessments of metal pollution from regulatory monitoring programmes and other research in the catchment. The study was novel due to the comprehensive monitoring of additional sites draining through spoil mine wastes. The deeper understanding of geological, biogeochemical and hydrological processes occurring in both point and diffuse sources provided relevant information about metal speciation and toxicity in the system. This integrated approach permitted an accurate assessment of metal pollution, providing evidence that metal carbonates present in spoil wastes were the major diffuse sources of pollution.

By including the assessment of the effect of episodic rainfall on metal mobility and toxicity this study has contributed a rich data set to assess water-quality trends, ecological risk, toxic effects and potential effectiveness of remediation technologies. Consistent with Jones et al. (2013), this study has shown that seasonal and episodic events had an increased effect on metal concentrations from spoil wastes, becoming a more challenging management problem than point source remediation. Based on the results, the most effective solution for mitigating metal pollution in Hebden Beck is spoil removal, although this is not a practical and cost-effective option. More likely alternatives to prevent diffuse pollution from spoil could be capping of the soil or possibly use of interceptor drains to divert drainage to a treatment system. Passive treatments have been also suggested by Baxter (2015), although remediation techniques need to be agreed through public participation (including residents), and should be considered alongside storm water management.

The present study concludes that metal assessment of catchments affected by mining is very complex, requiring the incorporation of *in situ* analytical approaches, speciation and toxicity modelling, bioavailability-based criteria and

active public participation to deal with appropriate ecological solutions. Contamination of water bodies in the UK by abandoned metal mines poses a serious barrier to the achievement of WFD objectives. This study provides useful scientific information about metal pollution in neutral mine drainage and suggests the incorporation of more rigorous methods based on bioavailable approaches (e.g. BLM, WHAM) for the assessment of chemical and ecological quality of surface water. In addition, this research offers baseline evidence to support current national initiatives for addressing community empowerment in water management for achieving the objectives of the WFD. Public perception of Hebden Beck's water quality revealed the necessity for better communication between non-specialist and specialist groups. Findings suggest that the community's understanding (especially residents) of existing scientific evidence about pollution issues in the catchment will be a crucial step for ensuring public engagement in metal mitigation solutions. Further research for understanding mechanisms of metal toxicity and bioavailability in neutral mine drainage might be beneficial to improve water quality standards and assist decision makers in readdressing environmental protection efforts where they are most needed. Likewise, social studies are essential for pursuing efficient involvement of the community in water-related issues and the achievement of an integrated catchment management encouraged by the EU-WFD and national policies.

In the following paragraphs I summarize the main findings of each analytical chapter and how they contributed to achieve the aims of this thesis.

6.1.1. Sources of metal pollution in Hebden Beck

Point and diffuse sources of metals were investigated through an extensive chemical analysis of river water, sediments and spoil wastes and the modelling of geochemical reactions occurring in the aqueous phase (Chapter 2). Chemical analysis showed significant Zn and Pb pollution as products of early mining activities, where diffuse sources were the major contributors. Geochemical modelling revealed the effects of weathering on carboniferous limestone bedrock and its influence in controlling pH and weathering reactions. Furthermore, by using metal-pH values, solubility of controlling metal-mineral phases were

predicted, demonstrating that carbonates and sulphides were the solid phases controlling the solubility of Pb and Zn. Moreover, weathering processes like dissolution of carbonates and oxidation of sulphides were considered the key reactions for producing high concentrations of Zn and Pb. These findings concur with other studies in the Yorkshire Pennine Orefield, UK. For instance, Jones et al. (2013) showed Zn and Pb as the main contaminants from a upland tributary of the River Wharfe, and Tame et al. (2017) indicated the evidence of secondary metal sources (particularly smithsonite) in headwater tributary of the River Swale. Analysis of sediments and spoils were consistent with water chemistry results showing Zn and Pb as significant pollutants present in spoils due to lower extraction efficiency methods common in historical mining. Exploring the kinetics of leaching from mineral forms in the spoils and sediments is recommended as future work. Overall, the information on sources of metals derived from geological and biogeochemical processes occurring in limestone areas gives an important understanding about the chemistry of neutral mine drainage in catchments affected by mining, which has to date only been partially studied.

6.1.2. Speciation and mobility of major metal pollutants

The speciation and mobility of metals were assessed by geochemical modelling (Chapter 2) and an *in situ* analytical approach known as DGT (Chapter 3). Geochemical modelling (PHREEQC) revealed the importance of secondary minerals such as carbonates, sulphates and hydroxides in the occurrence, hence mobility of dissolved metals. This study provides evidence that zinc is preferentially partitioned from sulphide dissolution and absorption by carbonate and bicarbonate ions derived from calcite weathering to form secondary zinc carbonate (smithsonite). For the case of Pb, it was also precipitated into a secondary mineral (cerussite) or complexed with Fe oxyhydroxide, becoming more insoluble than Zn in circumneutral waters. In addition, weathering of cerussite and smithsonite were important regulators for concentrations of Pb and Zn. However, Nordstrom (2011), stated that the mobility and speciation of metals not only depends on the sources, but also additional factors like biogeochemical and hydrological site-specific conditions (e.g. DOM, pH and flow). Thus, the

chemical speciation model (WHAM) was used for predicting the speciation of metals in the river water containing organic ligands. Predictions suggested that major toxic pollutants were present in different forms. Zn was mainly present as free ions and labile inorganic complexes, while Pb was present as less labile forms due to its complexation with organic compounds and colloids. Regarding pH conditions, circumneutal pH and buffering capacity were maintained by groundwater during base flow conditions (Chapter 2). However, Salomons and Förstner (2012) have mentioned that these conditions could be altered by rainfall (e.g. acid rain) and runoff, producing shifts in pH and allowing desorption of metals from spoils, sediments or soils (conditions that were evident in only a limited number of our monthly surveys). By using seasonal variations the effects of flow and pH in metal concentrations were estimated. In Hebden Beck a strong correspondence was identified between flow and Pb (r= 0.6), whereas flow-Zn relationship was unclear. Although, good correlation was observed in Zn-pH (r= 0.7) (Chapter 2). Studies from Byrne et al. (2009) and Cánovas et al. (2008) also indicated an effect of storm runoff in weathering metal salts from superficial mine spoils. Based on this background, a complementary assessment was performed to evaluate the concentrations and mobilisation of dissolved metals under different flow conditions such as episodic high rainfall (Chapter 4). Results revealed that episodic rainfall increased concentrations of dissolved metals, with a greater impact on Pb than Zn, but without altering the circumneutral conditions of the river. Similar results were obtained by Jones et al. (2013) and demonstrate that limestone-rich bedrock controls pH values in the river water (Chapter 2). Furthermore, it was observed that high episodic runoff produces faster weathering of calcite and secondary metal-carbonates, increasing the concentrations of carbonate and bicarbonate ions, affecting smithsonite dissolution (Chapter 4). These results agreed with Pokrovsky and Schott (2002) regarding the effects of circumneutral conditions in dissolution kinetics of smithsonite. Furthermore, the application of *in situ* monitoring tools (DGT) provided complementary information about the speciation and kinetics of Pb and Zn in the catchment (Chapter 3). Results revealed that Pb was likely complexed with DOM, forming colloids and reducing Pb mobility (diffusion coefficient), while

Zn was present as free ions or readily labile complexes, confirming previous predictions obtained with WHAM. Further research is recommended for DGT application under field conditions as discrepancies were observed in concentrations between metals measured in water and metals in devices, possibly due to a biological factor like biofouling and flow fluctuations decreasing the stirring rates, as previously reported by Davison and Zhang (1994) and Turner et al. (2014). Thus, it is suggested that the application of DGT under different flow regimes in water and sediments is considered, as this tool could provide more information about distribution and potential toxicity of metals to assess environmental impacts. Accordingly, Zhang and Davison (2015) suggested that the application of DGT under different environmental conditions needs more detailed studies in order to better resolve the uptake mechanism and kinetics of metals. For these reasons, Omanović et al. (2015) and Han et al. (2013) have used DGT techniques in combination with modelling approaches, based on data from toxicity tests.

6.1.3. Metal toxicity and bioavailability and their effects on river water quality.

Data from Chapter 2 and Chapter 3 were used to evaluate the river water quality by using ecotoxicology assessment techniques and established Environmental Quality Standards (EQS) for Pb and Zn. A preliminary assessment was carried out through the comparison of annual metal load estimations in the catchment with EQS (Chapter 2). Here, both metals showed maximum exceedances of 12-fold, with contributions of 0.2 tonne of Pb per year and 2.9 tonne of Zn per year. But several studies such as Smith et al. (2015) have demonstrated that metal toxicity and bioavailability are not just controlled by dissolved metal concentrations, but that other factors like pH, hardness, ionic strength, organic matter, and inorganic and organic colloids are also relevant. Thus, a secondary assessment was performed by including standards based on water hardness (EQS-H). Related research has indicated that water quality assessment only using standards based on water hardness (EQS-H) may be overly conservative as they fail to consider chemical speciation of metals and their environmental risk

(Merrington, 2016). Thus, we include a more rigorous approach based on bioavailability (EQS-B, WHAM and WHAM-F_{TOX}). Outcomes agreed with previous statements, showing that standards based on single metal concentrations and hardness conditions (EQS-H) were more conservative than tools that take account chemical speciation of metals (EQS-B, WHAM and WHAM-F_{TOX}). However, studies from Rüdel et al. (2015) have reported some limitations in the application of EQS-B, such as physicochemical parameters near or outside the established boundaries. For instance, in this study, EQS-Zn were estimated under mentioned limitations as pH and DOC were outside the established ranges (pH ≥6 and DOC ≤15 mg/l). Results from WHAM-F_{TOX} showed that metal toxic effects occurred at circumneutral pH. However, predicted maximum species diversity was reduced from 65% to 3% in eleven out of sixteen sites. Total metal toxicity (Zn^{2+} + Pb^{2+} + H^{+} + Al^{3+}) needs to be addressed with caution because Pb toxicity was calculated using a coefficient with a large degree of uncertainty (α_{Pb}= 2.51, p-value= 0.91) reported by Stockdale et al. (2010) in absence of an alternative published value. Despite modelling limitations, these tools are useful for having a holistic scenario of the water chemistry including interactions between metal mixtures and organisms. Finally, this study provided a practical context by comparing toxicity predictions from WHAM-F_{TOX} with results from an *in situ* macroinvertebrate survey. This appraisal revealed a relationship between increasing Zn concentrations and reduced diversity. Likewise invertebrate data showed that responses of species diversity and composition could be related to the influence of complex interactions between metals and acid scenarios (e.g. H13 and H4). Moreover, neutral mine drainage is likely to show different effects on macroinvertebrate communities. For instance, Clements et al. (2013) have indicated different tolerances of macroinvertebrate communities to pollution. Since the assessment only considered macroinvertebrate richness at family level, interpretations about the effect of metals on biota cannot be generalised. Hebden Beck has been affected by metal discharge for over 200 years and it is possible the ecosystem might have developed mechanisms to cope with this environment. However, the hydrological cycle is being altered increasingly by changes in climate, affecting the

remobilisation and deposition of metal-rich sediments and enhancing metal-rich runoff. Therefore, we studied the effects of episodic rainfall on concentrations and toxicity of metal fluxes derived from ephemeral and perennial tributaries, and the main river (Chapter 4). Calculations from WHAM and WHAM-F_{TOX} indicated that short term fluctuations in metal concentrations were not reflecting an acute toxicity risk to aquatic organisms. WHAM-F_{TOX} is parameterised only for macroinvertebrates (ephemeroptera, plecoptera and trichoptera), hence the integration of supplementary tools for assessing toxic effects in other ecological groups (e.g. zooplankton, algae and fish) will improve the utility of WHAM-F_{TOX} for site selection strategies dedicated for catchment clean-up. This rational assessment might support the prioritization of vulnerable sites where remedial action can be focused on reducing metal bioavailability for improving ecological endpoints. In general, an improved metal assessment requires the consideration of tools based on bioavailability. Further appraisals should focus on perennial tributaries from spoil runoff areas with potential ecological harmful levels of metals and under variable seasonal and episodic flow conditions.

6.1.4. Awareness of metal pollution in Hebden Beck

Legal frameworks for management of freshwaters have been established by policies based on technical and scientific knowledge, but leaving the role of society underestimated. Although all groups are generally keen to contribute to the formulation and effective implementation of resource management policies, the synergy between them is frequently poor. Thus, the management of freshwater needs to move from traditional approaches to more integrated initiatives. Chapter 5 looks to provide a foundation for negotiating differences and building common ground that can motivate cooperative environmental planning to improve Hebden Beck's water quality and is an example of how this could be implemented in other catchments. This last chapter sought to identify public awareness (residents, visitors and stakeholders-specialists) of river ecosystem services, perceptions of river water quality, opinions about flood effects and response to potential metal remediation practices. Outcomes indicated different perceptions on water quality between specialists and non-specialists, possibly

due to an inadequate transference of knowledge from technical to local community and potentially across stakeholder groups. In addition, it was observed that perceptions of Hebden Beck water quality from non-specialists (residents and visitors) are based on field observations (e.g. colour or odour). Regarding perception of mines, residents considered them as an important cultural legacy, while visitors were more aware of their latent pollution effects for the river, especially during heavy rainfall. Consequently, remediation strategies were more acceptable to visitors than residents, although the preferred approaches from both groups were passive systems to protect the landscape of the village and its surroundings. Based on these findings, Chapter 5 indicated the importance of consulting different stakeholder groups to understand their potential contribution to, and opinion of, management processes, and how best to integrate these contributions to achieve effective outcomes. These inferences agree with studies from Hu and Morton (2011) about understanding of people's general knowledge, awareness, and beliefs about water, discovering agreement as well as differing perspectives as the first step for creating an effective place-based assessment. Furthermore, as indicated by Potter et al. (2004) the remediation of diffuse pollution requires creative regulation and innovative approaches due to the difficulties associated with treatment at source. In Hebden Beck, passive remediation has been suggested as a potential approach (Baxter, 2015). Aside from the technical challenges, a critical factor in the success of remediation schemes will be the engagement with the community (especially residents). Thus, a clear translation of scientific and technical knowledge to the public is essential for a better understanding of chemical processes and potential ecological benefits, as well for supporting the protection of remediation structures or their regular maintenance (e.g. reporting vandalism, equipment malfunction).

6.2. Conclusions

In this thesis I presented a comprehensive study of the sources, mobility, speciation, toxicity and bioavailability of metals occurring in neutral mine drainage derived from historical mining in a carboniferous catchment. Analysing the river water, sediments and spoil revealed that geological, biogeochemical, and hydrological processes are controlling the river water chemistry, affecting the

mobility and speciation of different metal forms. In addition, the understanding of metal interactions with biotic and abiotic components provided a better knowledge of chemical speciation, including potential bioavailability and toxic effects. Furthermore, the evaluation of water quality assessment techniques offered a clearer understanding of the strength and weakness of current methods. By including both chemical speciation and ecological predictions this study has contributed extensive data, providing a more nuanced approach for toxicity and bioavailability assessment, especially for regulatory purposes. In addition, the appraisal of potential effects of climate change in producing metal-rich fluxes offered important insights for identifying key episodic rainfall-induced processes like deposition and remobilisation of metals, potentially reducing water quality. This timely analysis contributes considerably to the assessment of streams draining spoil waste areas with similar geochemical conditions and support future metal mitigation strategies and catchment management.

Moreover, the assessment of the public perceptions of river water quality outlined the role of each group associated with the studied catchment. This preliminary assessment provides a basis for conducting integrated water management. In addition, the understanding of water chemistry and metal processes under different seasonal and flow conditions offers the opportunity to propose efficient mining remediation schemes. Tributaries from diffuse (spoil) sources are the major contributors of metal pollution in this catchment, thus findings could be applied to other polluted catchments where tributaries drain mine spoils under similar conditions. In addition, regulatory agencies could use these findings for the implementation of a catchment based approach (CaBa) and the achievement of “good ecological” and “chemical status” under the EU Water Framework Directive or other national legislation.

6.3. Future directions

- This investigation has focussed mainly on metal assessment in river water and a limited number of spoil and sediments. Further studies including a more substantial investigation of solid phases including leaching studies will be beneficial for a better understanding of cycling of metals in the catchment.

- Further research is needed to compare field data and laboratory experiments (e.g. temperature, deployment time, and flow rates) to fully establish the applicability of DGTs regarding metal bioavailability in freshwaters.
- Studies about tolerance of macroinvertebrates to metal pollution in neutral mine drainage derived from historical polluted sites may clarify biota responses to long-term metal pollution. Likewise, these studies may add useful toxicity data (especially for Pb) to be incorporated in speciation and ecotoxicological modelling.
- In this study the assessment of episodic rainfall in metal toxicity was limited by hydrological characteristics of the site (ephemeral tributary). Therefore, it is suggested an additional assessment in a perennial tributary draining through spoil wastes, where ecologically harmful levels are known.
- Considering the community preference for passive remediation systems, projects like the pilot remediation in Cumbria at Force Crag (passive treatment system for metal mine drainage rich in Zn) could be explored to assess the applicability in Hebden Beck.
- For implementing an effective catchment management, social studies are recommended for identifying appropriate practices in the involvement of all interested parties.

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Appendices

Appendices-Chapter 2

Appendix 2. 1. Mean, maxima and minima from water chemical analysis. Sites are indicated as reservoir (RS), main channel (MC), ephemeral tributaries (ET) and perennial tributaries (PT). Metal forms are denoted as Total (T) and dissolved (D). Concentrations are expressed in μg/l. Values below the detection limit are represented by (b/d).

Site			Pb_T	Pb_D	Ba_T	Ba_D	Cd_T	Cd_D	Sr_T	Sr_D	Zn_T	Zn_D	Cu_T	Cu_D	Fe_T	Fe_D	Mn_T	Mn_D	Al_T	Al_D
H15	RS	Ave	316.7	279.6	293.8	288.1	6.4	6.4	25.8	26.9	2058.8	2028.0	12.3	12.4	562.9	406.4	69.3	70.9	383.8	341.1
		Max	411.9	423.6	570.4	465.5	8.2	8.6	37.8	46.0	2542.4	2759.5	19.6	19.9	2473.1	1622.1	201.7	202.4	522.5	428.7
		Min	96.3	103.6	165.2	173.5	3.1	4.3	15.9	14.1	722.4	1080.7	3.8	1.3	185.8	94.5	39.5	24.2	132.1	102.2
H14	PT	Ave	178.3	157.6	687.8	651.8	3.6	3.9	63.9	60.1	1318.6	1397.9	6.2	7.7	288.1	203.4	24.0	26.3	270.6	249.9
		Max	292.3	375.5	1195.3	1135.2	4.5	7.5	103.1	99.0	1778.9	2193.1	10.4	15.0	626.6	337.0	48.5	53.9	574.0	462.1
		Min	106.9	75.7	408.3	241.4	3.1	2.9	40.5	21.2	864.7	900.3	b/d	1.4	114.2	103.6	9.0	9.5	101.1	123.6
H13	ET	Ave	227.1	205.9	200.2	201.2	0.9	0.9	13.7	13.8	260.4	207.4	2.6	2.3	967.6	833.8	74.3	74.3	613.3	552.2
		Max	331.3	283.4	501.2	513.5	4.1	3.7	47.2	49.7	1619.8	1435.5	9.0	8.3	1451.9	1515.1	95.5	112.6	972.1	752.5
		Min	141.2	138.0	139.3	135.2	0.4	0.4	8.1	7.5	b/d	b/d	0.9	b/d	483.4	187.2	36.0	30.0	371.2	284.0
H12	ET	Ave	686.4	284.2	285.5	198.6	29.1	27.7	391.5	340.2	5168.8	4252.3	14.0	9.5	528.4	205.8	73.7	70.5	312.0	147.5
		Max	2701.2	439.9	419.4	285.4	45.7	47.0	737.3	602.1	12619.3	7438.4	25.9	19.8	1635.4	988.7	171.6	180.0	1277.4	506.2
		Min	261.8	184.1	183.0	148.1	0.6	0.5	8.9	8.6	66.5	73.6	2.2	2.0	84.6	62.6	22.6	19.1	82.7	55.0
H11	PT	Ave	64.0	31.6	143.9	111.8	1.7	2.6	40.6	52.8	295.7	410.5	2.5	2.0	1282.9	1017.2	100.7	98.2	103.1	91.5
		Max	765.6	355.2	604.8	181.7	21.7	35.9	207.6	372.5	3493.9	5276.2	18.8	14.6	2894.7	2404.3	613.7	633.3	190.2	181.9
		Min	3.7	b/d	65.3	68.0	b/d	0.02	9.9	10.5	b/d	b/d	b/d	b/d	258.6	142.3	28.4	24.6	b/d	34.5
H10	ET	Ave	108.1	80.7	441.1	415.0	1.6	1.6	67.0	63.4	468.8	444.4	2.8	2.7	632.3	434.8	54.2	48.4	188.8	147.0
		Max	268.1	145.2	933.8	956.2	2.2	2.3	123.6	133.8	787.4	777.0	8.3	6.7	1942.8	815.9	116.6	77.5	385.2	249.2
		Min	11.8	3.1	97.8	79.5	0.1	0.1	17.5	15.2	b/d	b/d	b/d	b/d	260.8	163.8	29.2	28.7	63.1	62.0
H9	PT	Ave	28.5	20.8	131.0	122.3	0.7	0.7	32.3	33.0	125.2	95.7	1.1	1.4	1448.8	1097.9	69.0	64.9	158.1	136.9
		Max	171.9	94.3	412.3	282.7	2.2	1.9	83.0	88.1	572.2	518.6	5.1	5.3	3028.1	2045.1	145.2	155.7	366.7	254.7
		Min	12.7	2.0	66.7	68.4	0.42	0.5	11.4	10.5	b/d	b/d	b/d	b/d	584.1	379.2	35.5	29.6	44.0	36.7
H8	ET	Ave	38.1	19.0	399.4	398.2	1.0	0.9	108.5	106.1	318.5	269.0	2.1	1.9	369.8	218.8	39.4	33.2	70.4	47.8
		Max	123.5	28.2	661.3	606.8	1.5	1.6	197.1	222.0	438.3	435.2	4.3	5.5	865.8	614.7	92.9	53.6	165.1	104.0
		Min	12.2	5.3	195.2	246.8	0.6	0.5	52.2	48.9	b/d	b/d	b/d	b/d	75.7	32.0	18.5	12.2	b/d	14.6

Appendix.2.1 (continued). Mean, maxima and minima from water chemical analysis. Sites are indicated as reservoir (RS), main channel (MC), ephemeral tributaries (ET) and perennial tributaries (PT). Metal forms are denoted as Total (T) and dissolved (D). Concentrations are expressed in μg/l. Values below the detection limit are represented by (b/d).

Site			Pb_T	Pb_D	Ba_T	Ba_D	Cd_T	Cd_D	Sr_T	Sr_D	Zn_T	Zn_D	Cu_T	Cu_D	Fe_T	Fe_D	Mn_T	Mn_D	Al_T	Al_D
H7	PT	Ave	7.7	4.3	218.9	220.2	16.6	16.6	834.8	809.4	3440.2	3220.5	5.5	2.5	386.0	40.2	52.6	54.9	21.3	12.4
		Max	21.1	47.7	258.1	268.8	22.6	23.6	1391.3	1156.0	5425.8	4312.3	11.7	5.6	860.4	189.2	66.6	73.5	39.0	37.0
		Min	0.8	b/d	179.6	186.3	10.4	11.5	425.5	436.4	2062.0	1936.7	1.3	0.1	49.8	18.3	33.6	31.8	b/d	b/d
H6	MC	Ave	60.4	49.4	307.1	308.7	2.5	2.5	104.8	105.8	537.6	510.2	1.9	2.2	596.2	471.7	44.6	43.0	123.3	113.4
		Max	102.0	85.6	549.3	557.0	3.6	3.6	283.0	298.5	664.1	674.1	3.5	5.9	914.4	822.4	84.9	90.7	223.9	212.4
		Min	20.5	13.8	187.4	180.2	1.7	1.7	38.7	36.5	468.3	390.2	b/d	b/d	218.4	142.7	22.4	19.9	33.5	27.6
H5	PT	Ave	60.4	54.3	209.3	213.7	5.0	5.1	223.1	228.3	883.5	867.2	2.5	2.4	82.5	46.3	6.6	6.0	87.0	74.6
		Max	132.3	157.8	238.4	235.0	6.6	6.8	348.8	370.2	1216.5	1206.0	5.1	6.3	154.1	152.0	9.9	11.7	185.1	223.2
		Min	17.1	10.0	173.5	176.9	4.0	3.9	146.6	149.3	688.0	613.5	b/d	b/d	43.4	5.4	4.8	3.9	b/d	11.2
H4	ET	Ave	8.3	4.4	91.6	78.0	0.2	0.2	9.4	9.2	b/d	b/d	0.8	1.6	1320.0	635.3	136.9	135.8	416.9	277.2
		Max	26.7	6.6	228.4	99.4	0.2	0.3	15.0	12.2	68.6	68.6	3.0	10.2	5331.3	1006.0	164.6	179.1	822.2	389.0
		Min	3.2	b/d	57.4	60.0	0.1	0.1	6.8	6.5	b/d	b/d	b/d	b/d	455.9	336.9	95.4	31.8	248.7	189.7
H3	PT	Ave	2.8	0.2	200.1	200.0	0.6	0.6	373.5	381.4	b/d	b/d	0.2	0.3	37.4	3.7	16.7	5.3	37.7	9.6
		Max	10.6	0.7	251.6	217.8	0.7	0.6	405.4	420.6	98.6	84.7	1.3	1.6	152.9	18.5	54.3	26.3	153.0	47.0
		Min	0.05	b/d	157.9	160.7	0.5	0.5	324.6	292.0	b/d	b/d	b/d	b/d	2.4	b/d	1.7	1.5	b/d	b/d
H2	MC	Ave	46.7	39.4	239.6	246.7	2.6	2.7	164.9	169.8	515.0	485.9	2.1	1.6	314.0	248.0	28.3	27.8	101.2	93.5
		Max	93.5	87.4	318.0	306.1	3.6	3.5	333.0	356.4	765.4	606.9	5.9	4.5	733.6	657.2	62.5	67.6	207.1	187.8
		Min	17.0	4.2	171.1	180.1	1.2	2.0	70.9	67.9	194.5	360.5	b/d	b/d	103.3	7.6	13.7	5.3	37.9	24.2
H1P	PT	Ave	3.0	1.9	199.7	200.5	0.1	0.09	51.9	53.1	b/d	b/d	1.1	0.7	317.9	205.4	27.9	9.6	85.1	58.6
		Max	5.2	8.3	285.4	261.5	0.2	0.2	69.9	70.2	68.6	68.5	3.8	3.00	779.1	583.3	57.2	36.0	179.1	140.9
		Min	0.8	b/d	112.3	120.5	0.1	0.02	30.7	29.5	b/d	b/d	b/d	b/d	134.9	29.3	7.9	2.7	31.4	16.0
H1	MC	Ave	31.1	16.6	221.5	217.4	1.3	1.1	129.1	132.4	217.5	158.9	1.5	1.1	328.6	185.1	39.9	22.0	103.7	70.2
		Max	146.8	43.7	272.1	267.5	2.1	1.4	209.3	220.3	375.9	302.9	4.5	4.3	1252.7	405.4	169.7	66.6	358.6	137.3
		Min	5.1	b/d	153.1	145.8	0.8	0.7	62.2	57.7	77.9	67.8	b/d	b/d	122.5	50.1	19.3	10.9	b/d	19.9

Appendix 2. 2. Mean, maxima and minima of major ions, dissolved inorganic and organic carbons. Description of sites are indicated as reservoir (RS), main channel (MC), ephemeral tributaries (ET) and perennial tributaries (PT). Units are in mg/l.

Sites	Description		Cations				Anions				Dissolved carbons	
			Ca_T	Ca_D	Mg_T	Mg_D	SO_4^{2-}	NO_3^-	PO_4^{3-}	Cl^-	DIC	DOC
H15	RS	Ave	7.9	8.3	0.6	0.6	3.5	1.3	0.003	7.2	3.8	12.4
		Max	12.0	14.7	0.9	0.9	7.5	2.9	0.01	13.8	9.3	21.2
		Min	5.0	5.1	0.5	0.5	1.3	0.001	0.0005	3.3	1.3	6.9
H14	PT	Ave	10.4	9.9	0.7	0.7	5.9	1.0	0.003	7.5	3.9	8.3
		Max	15.7	12.8	0.9	0.8	9.1	1.6	0.007	13.4	6.2	14.7
		Min	7.1	7.1	0.5	0.5	3.4	0.4	0.0005	4.5	2.1	4.2
H13	ET	Ave	2.9	3.0	0.5	0.5	3.6	1.1	0.02	7.9	0.9	16.8
		Max	8.7	9.1	0.7	0.7	6.2	2.1	0.03	13.0	2.0	26.5
		Min	1.8	1.9	0.4	0.3	1.3	0.2	0.0005	2.4	0.2	8.9
H12	ET	Ave	27.2	25.8	1.4	1.3	20.0	1.8	0.007	8.5	12.5	6.8
		Max	45.9	45.2	2.0	2.0	46.0	3.0	0.013	18.8	24.2	11.0
		Min	2.0	2.1	0.5	0.5	9.9	0.5	0.0005	3.4	4.9	2.0
H11	PT	Ave	7.4	8.5	1.2	1.2	3.0	1.5	0.02	7.5	4.0	16.3
		Max	13.7	25.4	2.3	2.2	8.4	6.4	0.05	11.8	10.6	31.2
		Min	2.3	2.2	0.5	0.6	1.3	0.001	0.01	3.8	0.8	6.4
H10	MC	Ave	13.5	15.0	0.94	1.0	4.9	1.6	0.01	7.8	8.2	10.3
		Max	28.5	30.1	1.9	1.9	9.6	4.0	0.05	12.9	18.9	20.9
		Min	4.5	4.2	0.5	0.6	3.1	0.01	0.0005	3.9	3.4	3.6
H9	PT	Ave	7.6	7.8	1.2	1.2	3.8	1.3	0.02	7.9	3.7	16.7
		Max	18.9	20.0	2.7	2.7	6.2	2.3	0.03	13.4	13.4	33.0
		Min	2.3	2.3	0.6	0.6	2.7	0.6	0.01	4.7	0.7	7.3
H8	ET	Ave	37.0	38.7	2.0	2.03	10.7	2.5	0.008	8.5	22.3	8.0
		Max	65.9	64.2	4.0	3.9	20.1	8.0	0.012	16.9	39.3	17.5
		Min	0.04	19.2	b/d	1.2	5.1	1.0	0.0005	2.9	10.2	3.8
H7	PT	Ave	41.5	41.5	5.4	5.4	24.9	2.3	0.002	7.5	27.2	1.2
		Max	55.1	55.0	6.9	6.9	31.0	4.6	0.01	11.0	36.1	3.1
		Min	25.0	24.6	3.6	3.6	16.9	1.0	0.0005	6.0	16.6	0.001
H6	MC	Ave	18.7	18.9	1.5	1.5	6.7	1.9	0.01	7.9	10.5	10.9
		Max	38.9	38.7	3.3	3.4	10.6	3.5	0.05	13.3	24.1	23.9
		Min	8.6	8.5	0.8	0.8	3.4	0.3	0.0005	4.8	3.7	3.3
H5	PT	Ave	46.2	45.8	4.1	4.0	12.8	12.3	0.01	7.6	27.8	3.1
		Max	58.4	57.0	5.3	5.5	18.0	40.2	0.01	9.7	35.1	7.7
		Min	37.6	36.3	3.1	3.1	7.4	6.3	0.0005	5.9	20.9	0.2
H4	ET	Ave	2.6	2.6	0.7	0.7	4.7	4.9	0.05	8.3	0.9	8.8
		Max	3.8	3.8	0.9	0.9	9.7	15.2	0.1	12.6	2.3	12.9
		Min	1.5	1.7	0.6	0.6	2.0	0.8	0.03	4.6	0.1	6.5
H3	PT	Ave	55.1	54.9	9.0	8.9	12.7	5.1	0.005	7.6	42.7	1.2
		Max	60.2	58.1	9.8	9.8	14.9	9.9	0.01	12.0	46.5	4.7
		Min	47.3	44.7	7.9	7.6	8.7	2.1	0.0005	5.3	36.3	0.001
H2	MC	Ave	32.0	31.9	3.5	3.4	9.4	9.5	0.007	8.0	18.8	7.5
		Max	53.6	54.9	6.3	6.6	15.2	17.7	0.01	12.3	33.2	22.3
		Min	16.2	16.3	1.6	1.6	4.5	1.9	0.0005	5.6	6.3	1.4
H1P	PT	Ave	28.1	27.8	1.9	1.9	7.2	17.8	0.1	10.1	13.6	9.2
		Max	37.8	36.3	2.4	2.4	14.5	36.7	0.1	17.9	19.3	24.6
		Min	16.7	16.4	1.3	1.3	3.0	0.001	0.05	7.0	5.9	3.1
H1	MC	Ave	32.8	34.5	4.1	4.3	8.3	3.3	0.05	10.5	22.7	7.7
		Max	48.5	48.4	7.7	8.0	10.7	5.5	0.2	17.2	34.9	19.6
		Min	20.7	19.9	1.8	1.8	4.5	1.7	0.0005	7.6	11.1	3.1

Appendix 2. 3. Correlation coefficients showing positive and negative relationships between metal forms (T: total, D: dissolved) and pH, EC, DIC, SO_4^{2-}, and DOC. Pearson correlation coefficient is denoted as r, p-value as p and confidence interval (95%) as CI.

	pH	EC	DIC	SO_4^{2-}	DOC
Pb_T	r= -0.02 p= .736 CI [-0.162 0.115]	r= -0.2 p= .003 CI [-0.341 -0.076]	r= -0.2 p= .003 CI [-0.338 -0.072]	r= 0.1 p= .438 CI [-0.084 0.192]	r= 0.1 p= .145 CI [-0.035 0.239]
Pb_D	r= -0.1 p= .084 CI [-0.257 0.016]	r= -0.4 p< .001 CI [-0.523 -0.291]	r= -0.4 p< .001 CI [-0.517 -0.284]	r= -0.1 p= .194 CI [-0.228 0.047]	r= 0.3 p< .001 CI [0.135 0.393]
Ba_T	r= 0.39 p<0.001 CI [0.265 0.502]	r= -0.01 p= 0.915 CI [-0.146 0.131]	r= 0.01 p= 0.879 CI[-0.128 0.149]	r= 0.02 p= 0.829 CI[-0.123 0.154]	r=-0.06 p= 0.439 CI[-0.192 0.084]
Ba_D	r= 0.43 p<0.001 CI[0.308 0.535]	r= 0.02 p= 0.739 CI[-0.115 0.162]	r= 0.05 p= 0.460 CI [-0.087 0.190]	r= 0.02 p= 0.826 CI [-0.123 0.154]	r= -0.11 p= 0.116 CI[-0.247 0.027]
Cd_T	r= 0.2 p= 0.021 CI [0.025 0.296]	r= 0.2 p= 0.037 CI [0.009 0.281]	r= 0.1 p= 0.134 CI [-0.032 0.242]	r= 0.7 p< 0.001 CI [0.614 0.759]	r= -0.2 p= 0.016 CI [-0.302 -0.032]
Cd_D	r= 0.2 p= 0.015 CI [0.034 0.304]	r= 0.1 p= 0.081 CI [-0.015 0.258]	r= 0.1 p= 0.195 CI [-0.047 0.228]	r= 0.7 p< 0.001 CI [0.561 0.723]	r= -0.2 p= 0.010 CI [-0.312 -0.043]
Sr_T	r= 0.3 p<0.001 CI [0.207 0.454]	r= 0.6 p<0.001 CI [0.506 0.684]	r= 0.6 p<0.001 CI [0.531 0.702]	r= 0.9 p<0.001 CI [0.833 0.901]	r= -0.5 p<0.001 CI [-0.590 -0.378]
Sr_D	r= 0.4 p<0.001 CI [0.235 0.478]	r= 0.6 p<0.001 CI [0.547 0.713]	r= 0.7 p<0.001 CI [0.568 0.728]	r= 0.9 p<0.001 CI [0.826 0.897]	r= -0.5 p<0.001 CI [-0.600 -0.391]
Zn_T	r= 0.2 p= 0.040 CI [0.006 0.278]	r= 0.1 p= 0.405 CI [-0.080 0.196]	r= 0.04 p= 0.586 CI [-0.100 0.176]	r= 0.6 p< 0.001 CI [0.503 0.682]	r= -0.2 p= 0.039 CI [-0.279 -0.007]
Zn_D	r= 0.2 p= 0.008 CI [0.051 0.319]	r= 0.1 p= 0.381 CI [-0.077 0.199]	r=0.04 p= 0.588 CI [-0.101 0.176]	r= 0.6 p<0.001 CI [0.517 0.692]	r= -0.2 p= 0.022 CI [-0.295 -0.024]
Cu_T	r= 0.03 p= 0.715 CI [-0.113 0.164]	r= -0.3 p< 0.001 CI [-0.389 -0.130]	r= -0.3 p< 0.001 CI [-0.408 -0.152]	r= 0.2 p= 0.027 CI [0.018 0.289]	r= 0.2 p= 0.001 CI [0.105 0.368]

Appendix 2.3 (continued). Correlation coefficients showing positive and negative relationships between metal forms (T: total, D: dissolved) and pH, EC, DIC, SO_4^{2-}, and DOC. Pearson correlation coefficient is denoted as r, p-value as p and confidence interval (95%) as CI.

	pH	EC	DIC	SO_4^{2-}	DOC
Cu_D	r= 0.04 p=0.622 CI [-0.104 0.173]	r= -0.3 p<0.001 CI [-0.381 -0.121]	r=-0.3 p<0.001 CI [-0.422 -0.169]	r=0.04 p=0.602 CI [-0.102 0.175]	r= 0.2 p=0.003 CI [0.073 0.339]
Fe_T	r= -0.3 p<0.001 CI [-0.440 -0.189]	r= -0.3 p<0.001 CI [-0.429 -0.177]	r= -0.4 p<0.001 CI [-0.549 -0.325]	r= -0.3 p<0.001 CI [-0.441 -0.191]	r= 0.5 p<0.001 CI [0.358 0.575]
Fe_D	r= -0.3 p<0.001 CI [-0.432 -0.180]	r= -0.5 p<0.001 CI [-0.576 -0.360]	r= -0.5 p<0.001 CI [-0.621 -0.420]	r= -0.5 p<0.001 CI [-0.574 -0.358]	r= 0.7 p<0.001 CI [0.638 0.776]
Mn_T	r= -0.3 p<0.001 CI [-0.420 -0.167]	r= -0.2 p=0.007 CI [-0.319 -0.050]	r= -0.3 p<0.001 CI [-0.449 -0.201]	r= -0.2 p=0.011 CI [-0.312 -0.042]	r= 0.2 p=0.001 CI [0.102 0.365]
Mn_D	r= -0.3 p<0.001 CI [-0.437 -0.187]	r= -0.2 p=0.003 CI [-0.337 -0.071]	r= -0.4 p<0.001 CI [-0.464 -0.219]	r=-0.2 p=0.028 CI [-0.288 -0.016]	r= 0.2 p=0.001 CI [0.106 0.368]
Ca_T	r= 0.6 p<0.001 CI [0.493 0.675]	r= 0.9 p<0.001 CI [0.838 0.904]	r= 0.9 p<0.001 CI [0.951 0.972]	r= 0.7 p<0.001 CI [0.583 0.738]	r= -0.6 p<0.001 CI [-0.698 -0.525]
Ca_D	r= 0.6 p<0.001 CI [0.526 0.698]	r= 0.9 p<0.001 CI [0.845 0.908]	r= 0.9 p<0.001 CI [0.963 0.978]	r= 0.7 p<0.001 CI [0.571 0.730]	r= -0.6 p<0.001 CI [-0.701 -0.529]
Al_T	r= -0.6 p<0.001 CI [-0.644 -0.451]	r= -0.4 p<0.001 CI [-0.545 -0.320]	r= -0.6 p<0.001 CI [-0.658 -0.470]	r=-0.4 p<0.001 CI [-0.465 -0.220]	r= 0.4 p<0.001 CI [0.226 0.470]
Al_D	r=-0.6 p<0.001 CI [-0.690 -0.515]	r= -0.6 p<0.001 CI [-0.646 -0.454]	r= -0.7 p<0.001 CI [-0.731 -0.572]	r= -0.4 p<0.001 CI [-0.542 -0.316]	r= 0.5 p<0.001 CI [0.417 0.619
Mg_T	r= 0.4 p<0.001 CI [0.315 0.542]	r= 0.8 p<0.001 CI [0.782 0.869]	r= 0.9 p<0.001 CI [0.899 0.941]	r= 0.6 p<0.001 CI [0.472 0.660]	r= -0.6 p<0.001 CI [-0.657 -0.469]
Mg_D	r= 0.4 p<0.001 CI [0.322 0.547]	r= 0.8 p<0.001 CI [0.787 0.872]	r= 0.9 p<0.001 CI [0.897 0.939]	r= 0.6 p<0.001 CI [0.463 0.653]	r= -0.6 p<0.001 CI [-0.651 -0.461]

Appendix 2. 4. Monthly averages of *in situ* parameters in the catchment.

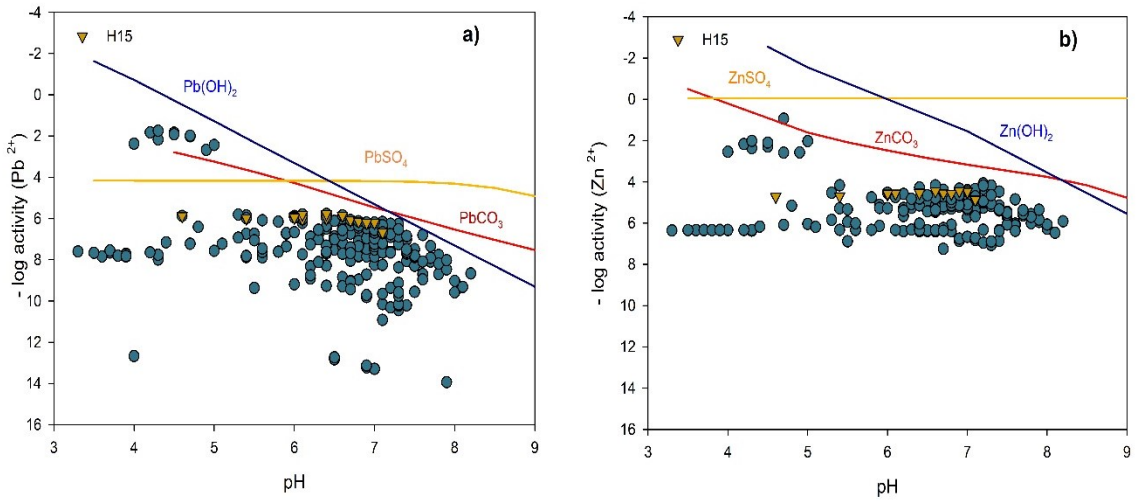
Months	Temp (°C)	DO (mg/l)	pH	EC (µs/cm)	Flow (l/s)
Nov.13	7.6 (±0.8)	11.4 (±0.4)	5.6 (±0.8)	94.0 (±58.8)	NM
Dec.13	9.0 (±0.6	10.2 (±0.3)	6.0 (±1.0)	99.9 (±68.8)	310.5 (±638.8)
Jan.14	5.0 (±1.4)	12.1 (±0.8)	6.1 (±1.1)	87.9 (±57.0)	250.2 (±422.8)
Feb.14	3.6 (±1.2)	12.5 (±0.9)	5.9 (±1.1)	78.0 (±43.1)	699.4 (±1365.1)
Mar.14	7.3 (±0.8)	12.3 (±1.1)	6.5 (±0.9)	120.4 (±65.7)	129.4 (±343.0)
Apr.14	8.5 (±1.7)	11.9 (±1.0)	6.6 (±1.1)	123.5 (±64.3)	62.9 (±146.8)
May.14	8.9 (±1.3)	12.6 (±0.9)	6.6 (±1.0)	137.3 (±70.8)	79.2 (±206.1)
Jun.14	13.7 (±2.8)	10.9 (±0.7)	6.6 (±1.1)	138.7 (±75.4)	98.9 (±233.9)
Jul.14	15.6 (±2.6)	10.3 (±0.6)	7.0 (±1.0)	209.0 (±82.3)	54.0 (±114.3)
Aug.14	13.0 (±1.8)	11.7 (±0.8)	6.4 (±1.4)	123.8 (±85.0)	389.8 (±954.3)
Sep.14	12.4 (±1.9)	14.0 (±1.2)	7.1 (±1.0)	154.3 (±71.0)	71.1 (±157.6)
Oct.14	9.7 (±1.1)	10.4 (±0.5)	6.6 (±1.0)	119.5 (±66.8)	107.3 (±183.4)
Nov.14	9.2 (±0.4)	10.4 (±0.5)	6.6 (±1.0)	99.9 (±59.0)	2666.1 (±10243.7)
Dec.14	4.2 (±1.2)	12.6 (±1.1)	6.8 (±0.8)	93.2 (±54.0)	292.1 (±568.8)

NM: No measured

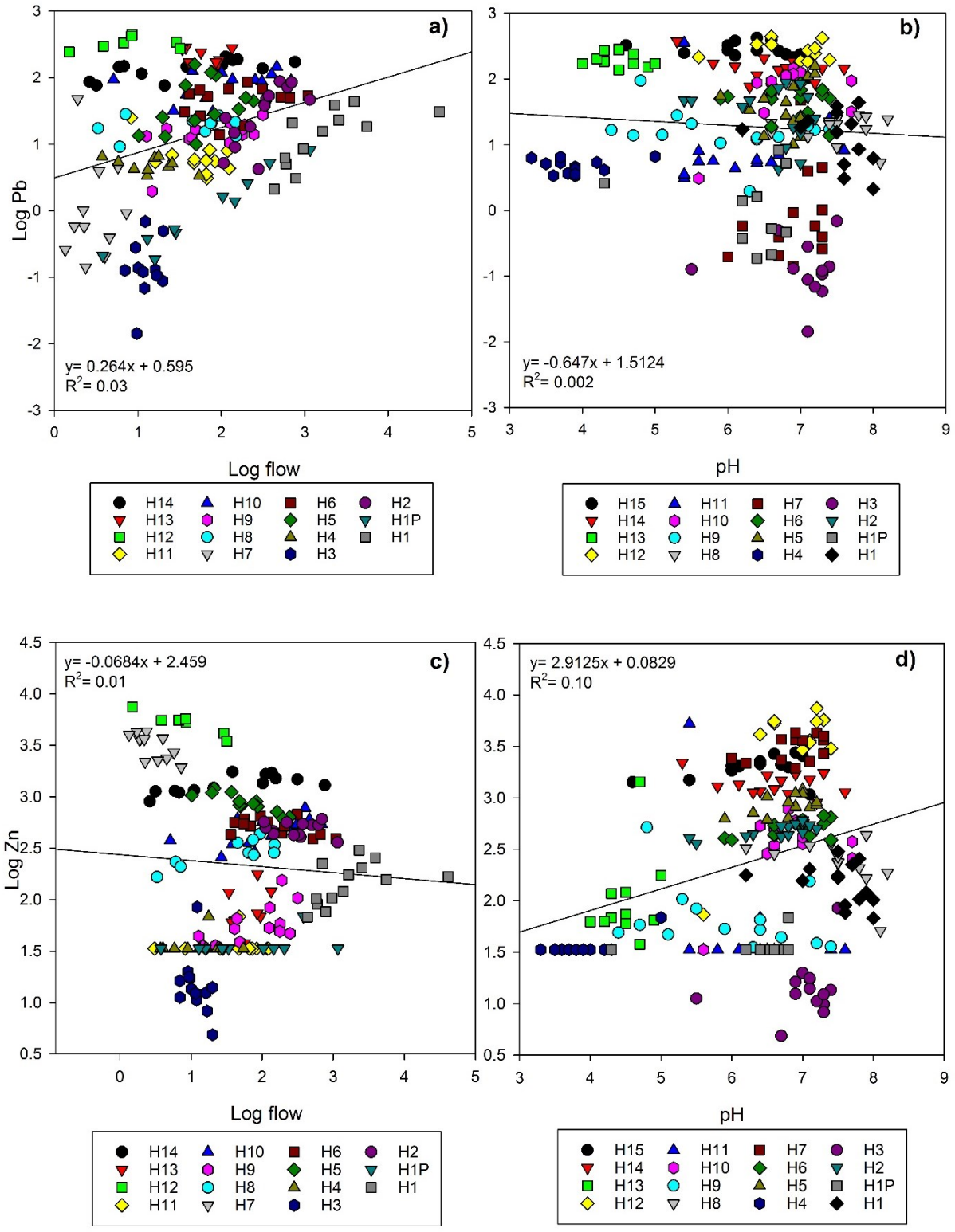
Appendix 2. 5. Averages, maxima and minima of *in situ* parameters. Description of sites are indicated as reservoir (RS), main channel (MC), ephemeral tributaries (ET) and perennial tributaries (PT).

Sites	Description		pH	EC (µs/cm)	Temperature (°C)	DO (mg/l)	Flow (l/s)
H15	RS	Ave	6.3	52.4	9.7	11.1	NM
		Max	7.1	95.4	18.5	13.2	NM
		Min	4.6	35.3	1.4	9.2	NM
H14	PT	Ave	6.6	59.4	10.0	11.5	128.5
		Max	7.6	99.9	18.3	13.1	761.7
		Min	5.3	41.1	3.0	9.5	2.6
H13	ET	Ave	4.5	48.9	8.4	11.0	57.0
		Max	5.0	65.2	15.7	13.1	134.4
		Min	4.0	35.6	3.7	9.1	0.0
H12	ET	Ave	6.9	123.7	8.9	11.5	9.0
		Max	7.4	199.7	18.0	13.2	31.9
		Min	5.6	64.9	2.8	10.0	0.0
H11	PT	Ave	6.2	47.8	6.9	11.8	57.4
		Max	7.6	100.4	11.0	13.3	123.6
		Min	5.4	30.0	2.0	9.5	3.1
H10	MC	Ave	6.8	76.0	9.7	12.2	200.2
		Max	7.7	160.3	18.8	14.2	684.4
		Min	5.6	46.8	4.1	10.0	5.1
H9	PT	Ave	5.9	52.3	9.2	12.0	118.8
		Max	7.4	107.5	17.9	14.8	315.0
		Min	4.4	36.7	3.7	10.0	12.8
H8	ET	Ave	7.4	152.1	9.1	12.1	51.3
		Max	8.2	303.0	16.9	15.7	149.3
		Min	6.2	75.8	2.2	9.8	0.0
H7	PT	Ave	6.9	192.4	9.1	10.9	3.0
		Max	7.3	292.0	11.9	13.9	7.3
		Min	6.0	112.0	5.1	9.5	0.6
H6	MC	Ave	6.9	94.7	8.7	12.4	265.0
		Max	7.4	253.0	16.9	15.4	1087.3
		Min	5.9	48.4	3.6	10.4	36.3
H5	PT	Ave	6.8	185.1	8.5	10.7	83.1
		Max	7.2	269.0	12.8	13.9	243.2
		Min	5.9	138.4	4.8	9.5	10.3
H4	ET	Ave	3.9	121.1	8.0	12.2	14.3
		Max	5.0	342.0	14.5	14.6	54.3
		Min	3.3	50.8	2.1	10.2	0.0
H3	PT	Ave	7.0	248.2	8.6	10.9	12.4
		Max	7.5	295.0	11.5	14.0	20.1
		Min	5.5	186.9	5.7	9.6	6.9
H2	MC	Ave	6.6	146.2	8.1	12.2	386.1
		Max	7.2	288.0	12.8	15.1	1147.0
		Min	5.4	76.0	3.2	10.0	106.6
H1P	PT	Ave	6.3	133.0	8.8	12.2	192.7
		Max	6.8	218.3	14.5	14.2	1162.2
		Min	4.3	71.9	3.5	10.0	3.8
H1	MC	Ave	7.5	159.8	10.6	11.5	4804.9
		Max	8.0	264.0	16.9	12.8	41076.0
		Min	6.2	90.9	4.5	10.1	432.0

NM: No measured



Appendix 2. 6. Lead and Zn activity as a function of pH, SO_4^{2-} (13592 μg/l), Cl (7730 μg/l) and pCO_2 = 0.0012 atm. Theoretical saturation of mineral forms are represented by solid lines and calculated metal free ion activity of experimental data by dots. Data from a source pond (H15) is shown separately as an example of how longer water residence times may result in free ion activities closer to saturation.

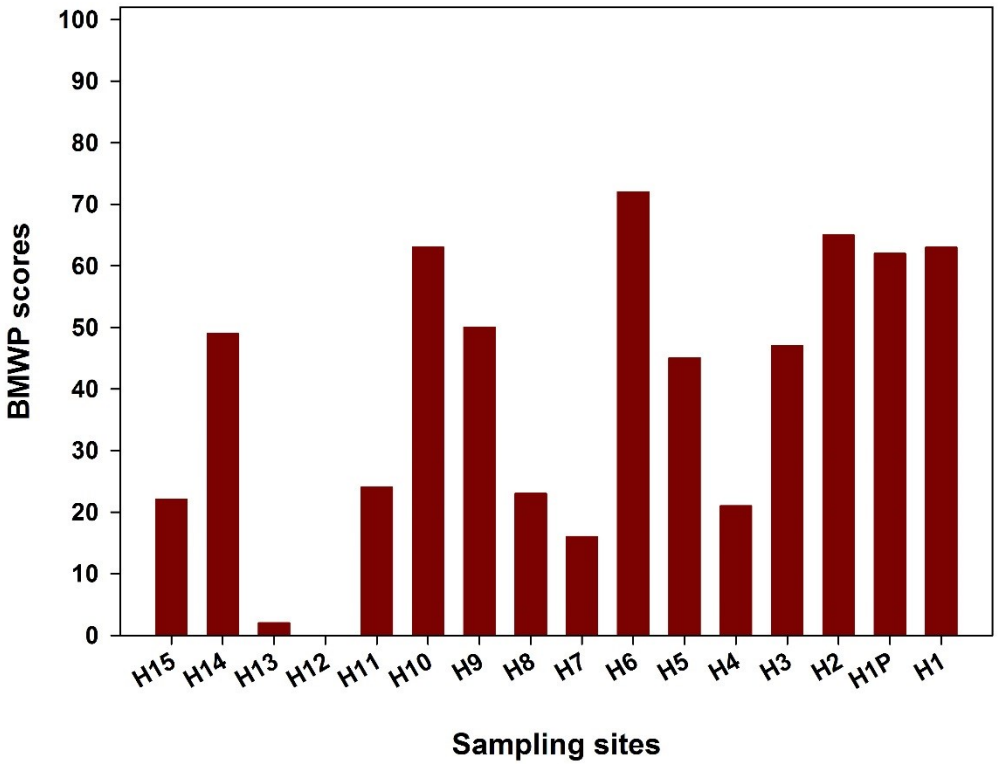


Appendix 2. 7. Trends of metals in function of flow and pH in all sampling sites. Panel a and b show trends of Pb and panel c and d indicate Zn trends. Flow data from H15 (reservoir) were not measured. Solid lines represent regression lines.

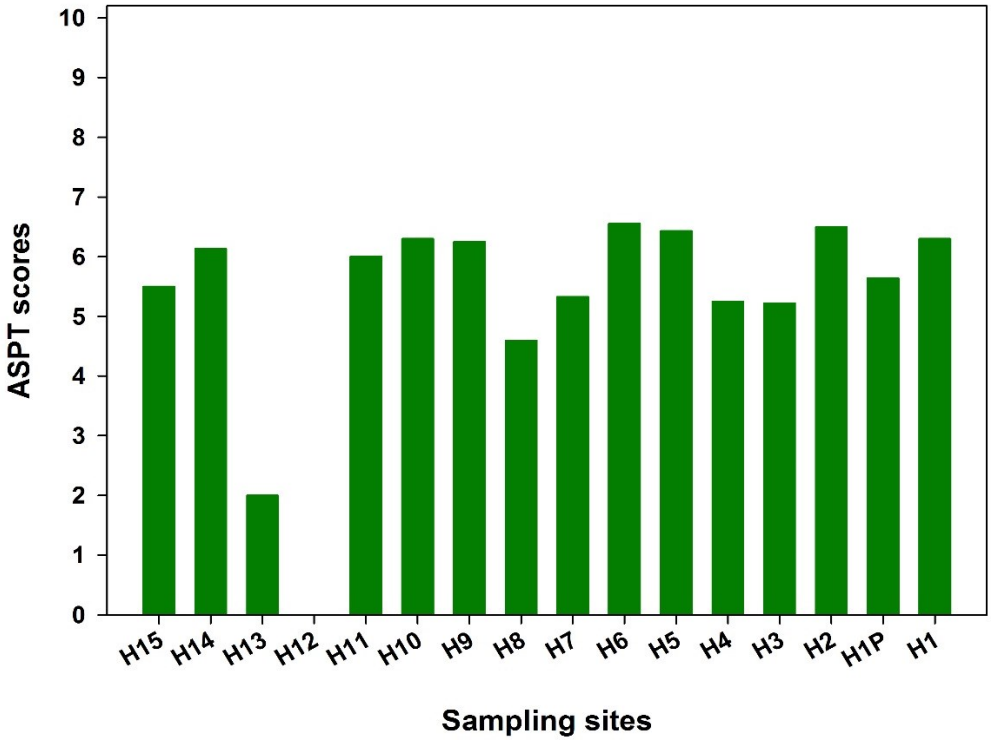
Appendices-Chapter 3

Appendix 3. 1. Annual averages and standard deviation (±SD) of metal-C_{DGT} concentrations at each sampling site. Units are in mol/l.

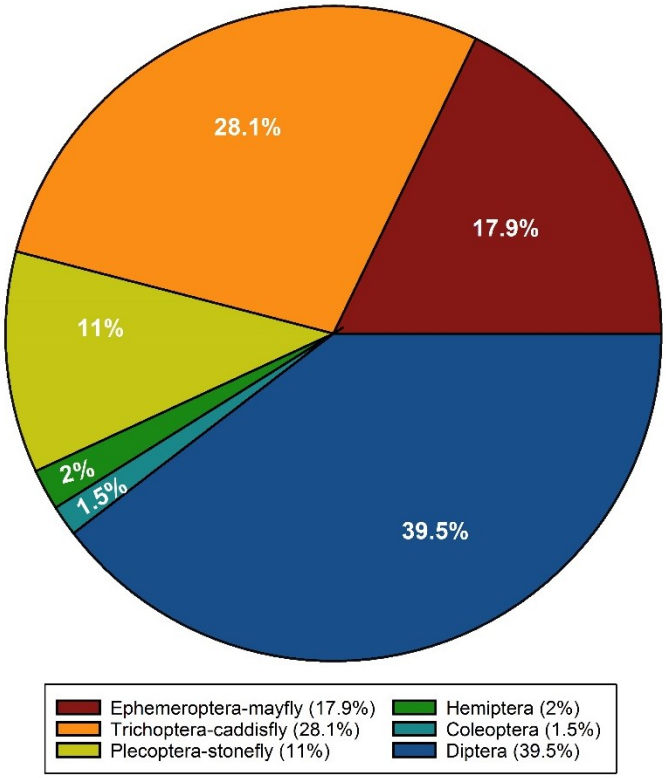
Sites	Zn_D_ measured (mol/l)	Zn_C_{DGT} (mol/l)	Pb_D_ measured (mol/l)	Pb_C_{DGT} (mol/l)	Cu_D_ measured (mol/l)	Cu_C_{DGT} (mol/l)	Cd_D_ measured (mol/l)	Cd_C_{DGT} (mol/l)
H15	$3.1x10^{-5}$ $\pm7.2\times10^{-6}$	$1.2x10^{-5}$ $\pm6.9x10^{-6}$	$1.3x10^{-6}$ $\pm2.9x10^{-7}$	$1.3x10^{-6}$ $\pm4.0x10^{-7}$	$1.9x10^{-7}$ $\pm5.9x10^{-8}$	$1.5x10^{-8}$ $\pm3.2x10^{-9}$	$2.4x10^{-6}$ $\pm5.3x10^{-7}$	$2.2x10^{-9}$ $\pm3.8x10^{-9}$
H14	$2.1x10^{-5}$ $\pm5.2x10^{-6}$	$1.5x10^{-5}$ $\pm4.4x10^{-6}$	$6.5x10^{-7}$ $\pm1.3x10^{-7}$	$7.6x10^{-7}$ $\pm3.6x10^{-7}$	$1.1x10^{-7}$ $\pm2.8x10^{-8}$	$1.8x10^{-8}$ $\pm9.8x10^{-9}$	$1.2x10^{-6}$ $\pm2.4x10^{-7}$	$1.2x10^{-9}$ $\pm9.4x10^{-10}$
H13	$3.2x10^{-6}$ $\pm6.3x10^{-6}$	$6.1x10^{-7}$ $\pm3.2x10^{-7}$	$1.0x10^{-6}$ $\pm2.7x10^{-7}$	$9.9x10^{-7}$ $\pm2.6x10^{-7}$	$3.0x10^{-8}$ $\pm1.9x10^{-8}$	$6.5x10^{-9}$ $\pm7.3x10^{-9}$	1.9x10-6 $\pm5.0x10^{-7}$	$2.0x10^{-9}$ $\pm1.3x10^{-9}$
H12	$6.5x10^{-5}$ $\pm3.0x10^{-5}$	$2.7x10^{-5}$ $\pm4.0x10^{-6}$	$1.6x10^{-6}$ $\pm4.0x10^{-7}$	$1.4x10^{-6}$ $\pm4.4x10^{-7}$	$1.9x10^{-7}$ $\pm9.1x10^{-8}$	$2.5x10^{-8}$ $\pm1.1x10^{-8}$	$2.9x10^{-6}$ $\pm7.4x10^{-7}$	$1.3x10^{-10}$ $\pm1.1x10^{-10}$
H11	$6.3x10^{-6}$ $\pm2.1x10^{-5}$	$3.3x10^{-6}$ $\pm7.6x10^{-6}$	$3.2x10^{-8}$ $\pm2.1x10^{-8}$	$1.5x10^{-7}$ $\pm4.5x10^{-7}$	$1.4x10^{-8}$ $\pm1.4x10^{-8}$	$1.1x10^{-8}$ $\pm1.4x10^{-8}$	$6.0x10^{-8}$ $\pm4.0x10^{-8}$	$1.4x10^{-9}$ $\pm8.8x10^{-10}$
H10	$6.8x10^{-6}$ $\pm2.8x10^{-6}$	$5.2x10^{-6}$ $\pm2.5x10^{-6}$	$4.0x10^{-7}$ $\pm1.4x10^{-7}$	$3.8x10^{-7}$ $\pm2.0x10^{-7}$	$4.4x10^{-8}$ $\pm2.0x10^{-8}$	$6.8x10^{-9}$ $\pm6.3x10^{-9}$	$7.5x10^{-7}$ $\pm2.7x10^{-7}$	$2.0x10^{-9}$ $\pm1.6x10^{-9}$
H9	$1.5x10^{-6}$ $\pm1.9x10^{-6}$	$1.3x10^{-6}$ $\pm5.5x10^{-7}$	$7.1x10^{-8}$ $\pm2.1x10^{-8}$	$1.0x10^{-7}$ $\pm1.1x10^{-7}$	$1.6x10^{-8}$ $\pm1.1x10^{-8}$	$6.2x10^{-9}$ $\pm8.4x10^{-9}$	$1.3x10^{-7}$ $\pm3.8x10^{-8}$	$1.7x10^{-9}$ $\pm1.1x10^{-9}$
H8	$4.1x10^{-6}$ $\pm1.5x10^{-6}$	$3.9x10^{-6}$ $\pm2.3x10^{-6}$	$9.2x10^{-8}$ $\pm2.1x10^{-8}$	$9.2x10^{-8}$ $\pm3.2x10^{-8}$	$2.8x10^{-8}$ $\pm1.9x10^{-8}$	$7.1x10^{-9}$ $\pm3.4x10^{-9}$	$1.7x10^{-7}$ $\pm3.8x10^{-8}$	$7.6x10^{-10}$ $\pm5.1x10^{-10}$
H7	$4.9x10^{-5}$ $\pm1.3x10^{-5}$	$2.8x10^{-5}$ $\pm8.5x10^{-6}$	$2.2x10^{-8}$ $\pm4.5x10^{-8}$	$2.1x10^{-8}$ $\pm6.1x10^{-8}$	$3.9x10^{-8}$ $\pm1.7x10^{-8}$	$1.6x10^{-8}$ $\pm2.9x10^{-9}$	$4.2x10^{-8}$ $\pm8.3x10^{-8}$	$1.2x10^{-10}$ $\pm7.3x10^{-11}$
H6	$7.8x10^{-6}$ $\pm1.5x10^{-6}$	$7.5x10^{-6}$ $\pm1.0x10^{-6}$	$2.2x10^{-7}$ $\pm9.7x10^{-8}$	$2.4x10^{-7}$ $\pm9.9x10^{-8}$	$3.3x10^{-8}$ $\pm2.4x10^{-8}$	$6.0x10^{-9}$ $\pm2.7x10^{-9}$	$4.2x10^{-7}$ $\pm1.8x10^{-7}$	$1.3x10^{-9}$ $\pm1.0x10^{-9}$
H5	$1.3x10^{-5}$ $\pm2.9x10^{-6}$	$1.3x10^{-5}$ $\pm1.5x10^{-6}$	$2.2x10^{-7}$ $\pm1.5x10^{-7}$	$2.6x10^{-7}$ $\pm2.2x10^{-7}$	$3.7x10^{-8}$ $\pm2.9x10^{-8}$	$8.0x10^{-9}$ $\pm4.4x10^{-9}$	$3.3x10^{-7}$ $\pm2.7x10^{-7}$	$1.8x10^{-10}$ $\pm1.2x10^{-10}$
H4	$5.5\ x10^{-7}$ $\pm1.4\times10^{-7}$	$2.6x10^{-7}$ $\pm8.9x10^{-8}$	$2.0x10^{-8}$ $\pm6.3x10^{-9}$	$2.1x10^{-8}$ $\pm8.2x10^{-9}$	$2.5x10^{-8}$ $\pm3.3x10^{-8}$	$2.1x10^{-9}$ $\pm1.1x10^{-9}$	$3.7x10^{-8}$ $\pm1.1x10^{-8}$	$9.6x10^{-9}$ $\pm1.1x10^{-8}$
H3	$<5.1\times10^{-7}$ -	$1.2x10^{-6}$ $\pm5.1x10^{-8}$	$6.3x10^{-10}$ $\pm3.9x10^{-10}$	$8.0x10^{-10}$ $\pm9.5x10^{-10}$	$4.5x10^{-9}$ $\pm5.4x10^{-9}$	$2.3x10^{-9}$ $\pm1.0x10^{-9}$	$1.1x10^{-9}$ $\pm7.1x10^{-10}$	$2.2x10^{-10}$ $\pm2.6x10^{-10}$
H2	$7.4x10^{-6}$ $\pm1.1x10^{-6}$	$7.0x10^{-6}$ $\pm1.0x10^{-6}$	$1.7x10^{-7}$ $\pm1.0x10^{-7}$	$1.9x10^{-7}$ $\pm1.4x10^{-7}$	$2.8x10^{-8}$ $\pm1.5x10^{-8}$	$4.2x10^{-9}$ $\pm1.9x10^{-9}$	$3.2x10^{-7}$ $\pm2.0x10^{-7}$	$9.8x10^{-10}$ $\pm7.6x10^{-10}$
H1P	5.6×10^{-7} $\pm1.1\times10^{-6}$	$4.8x10^{-9}$ $\pm4.5x10^{-9}$	$3.5x10^{-9}$ $\pm3.1x10^{-9}$	$3.5x10^{-9}$ $\pm3.1x10^{-9}$	$1.3x10^{-8}$ $\pm1.2x10^{-8}$	$3.8x10^{-9}$ $\pm2.6x10^{-9}$	$6.4x10^{-9}$ $\pm5.8x10^{-9}$	$8.9x10^{-11}$ $\pm9.0x10^{-11}$
H1	$2.4x10^{-6}$ $\pm1.1x10^{-6}$	$2.5x10^{-6}$ $\pm6.6x10^{-7}$	$6.4x10^{-8}$ $\pm4.9x10^{-8}$	$8.0x10^{-8}$ $\pm6.6x10^{-8}$	$1.9x10^{-8}$ $\pm1.4x10^{-8}$	$3.8x10^{-9}$ $\pm2.2x10^{-9}$	$1.1x10^{-7}$ $\pm9.2x10^{-8}$	$8.1x10^{-7}$ $\pm9.4x10^{-10}$



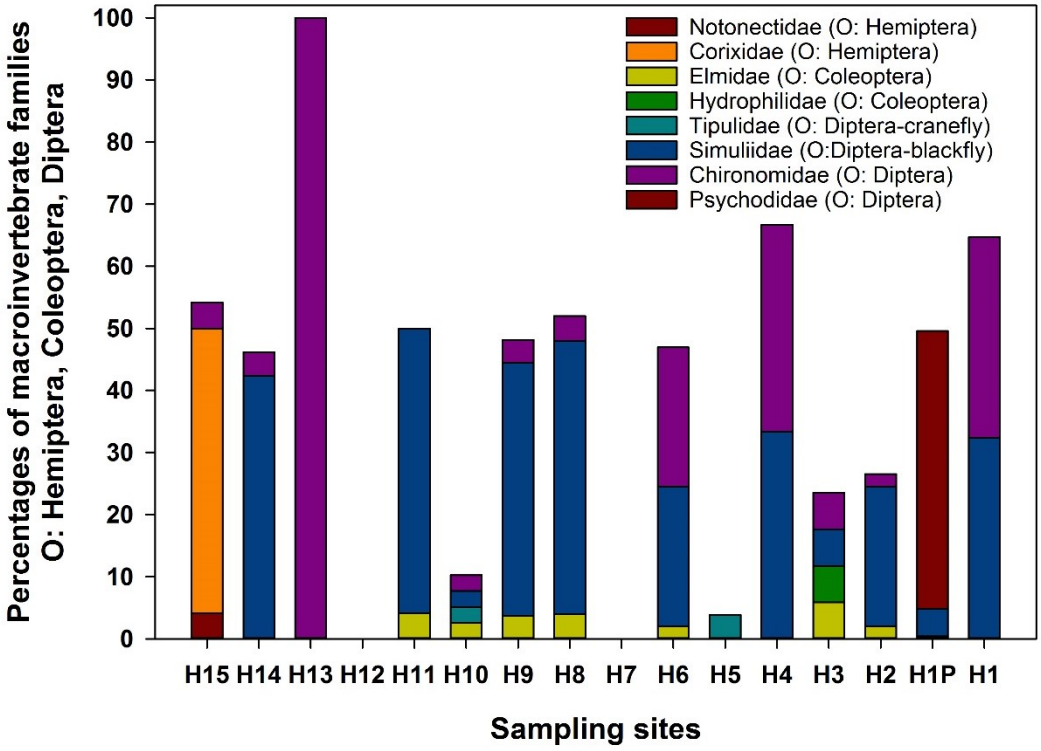
Appendix 3. 2. Biological Monitoring Working Party (BMWP) scores based on macroinvertebrate presence at each sampling site.



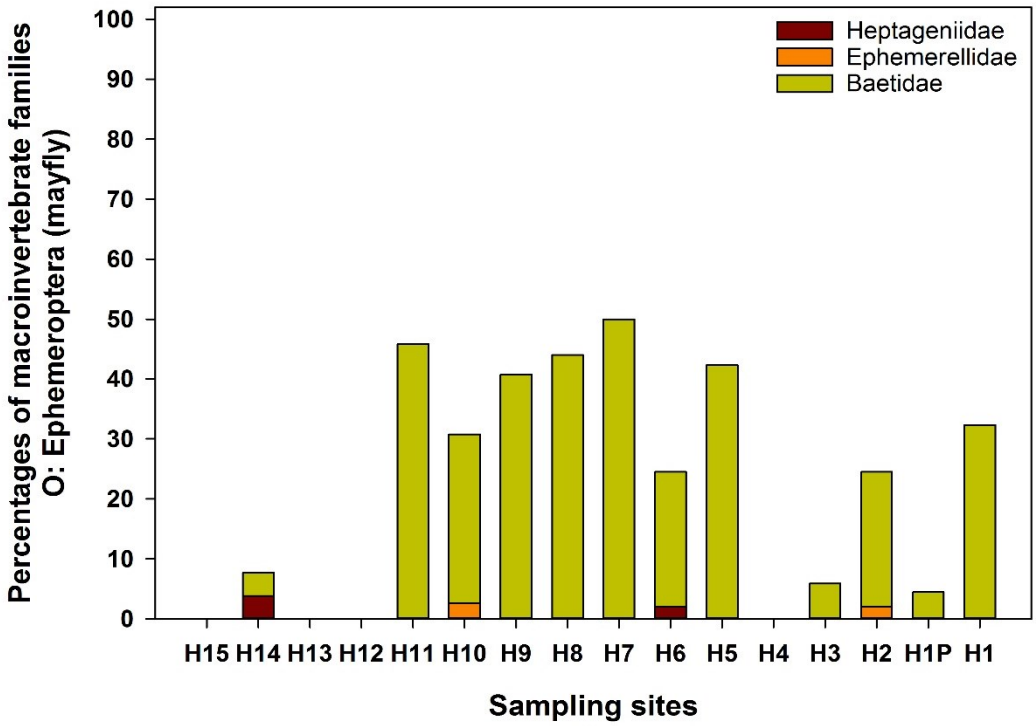
Appendix 3. 3. Average scores per taxon (ASPT) at each sampling site.



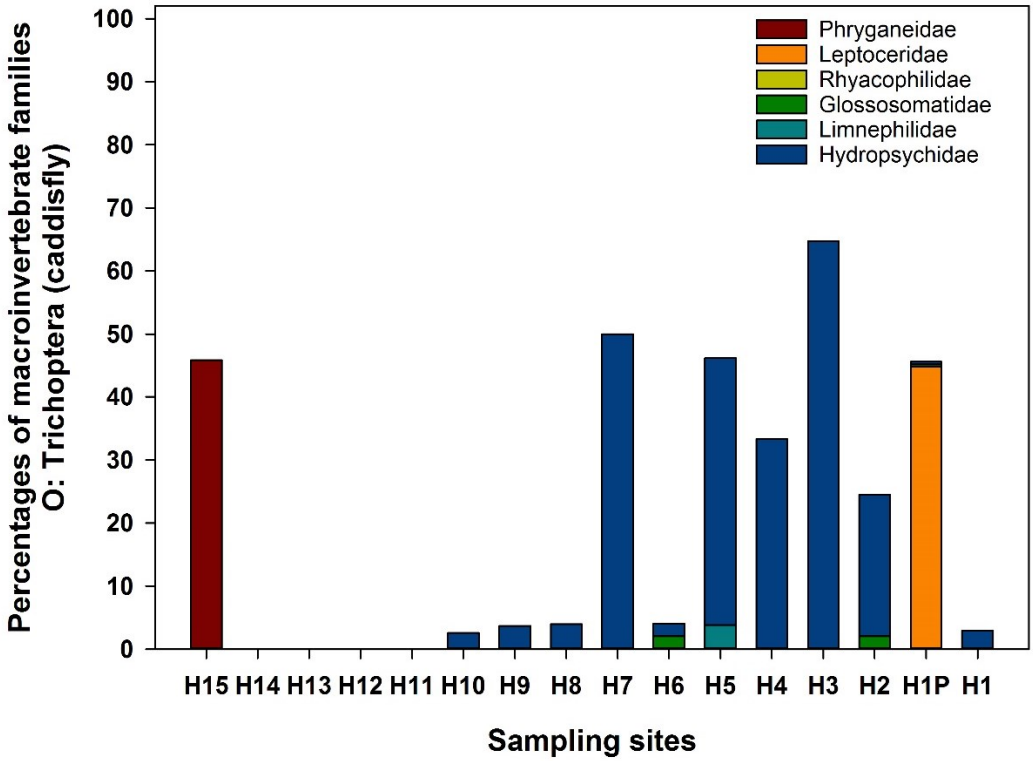
Appendix 3. 4. Percentages of each macroinvertebrate order based on number of individuals.



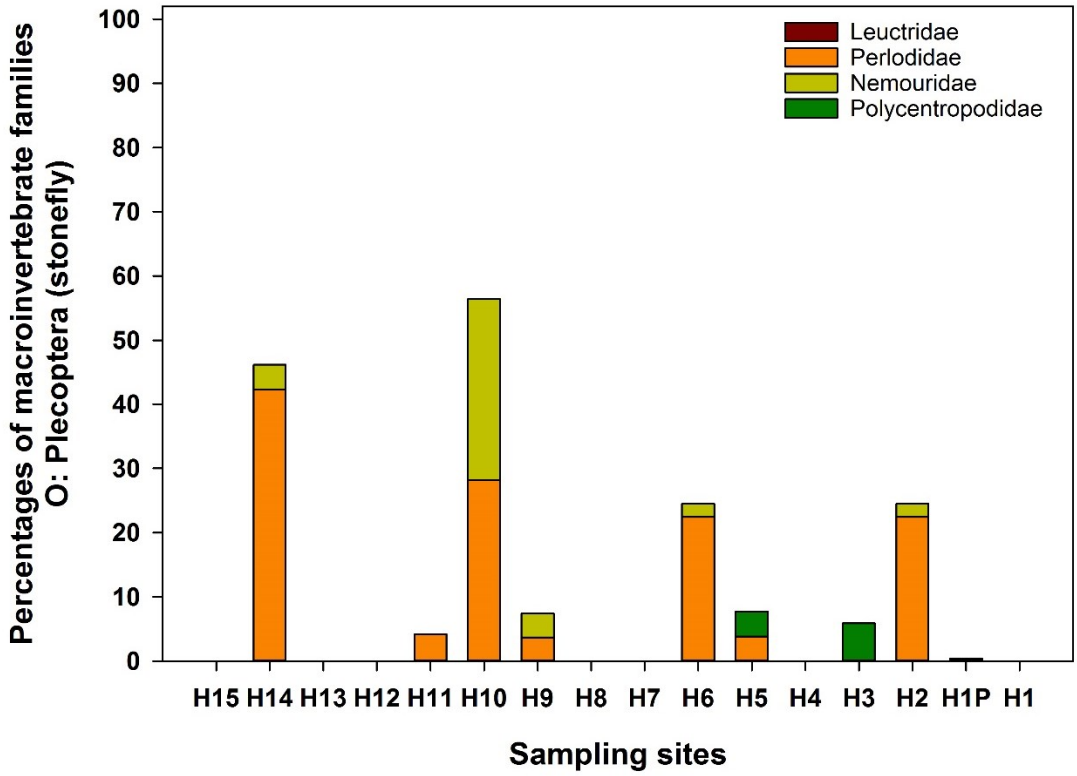
Appendix 3. 5. Percentages of macroinvertebrate families from the Orders Hemiptera, Coleoptera and Diptera.



Appendix 3. 6. Percentages of macroinvertebrate families from the Order Ephemeroptera (mayfly).



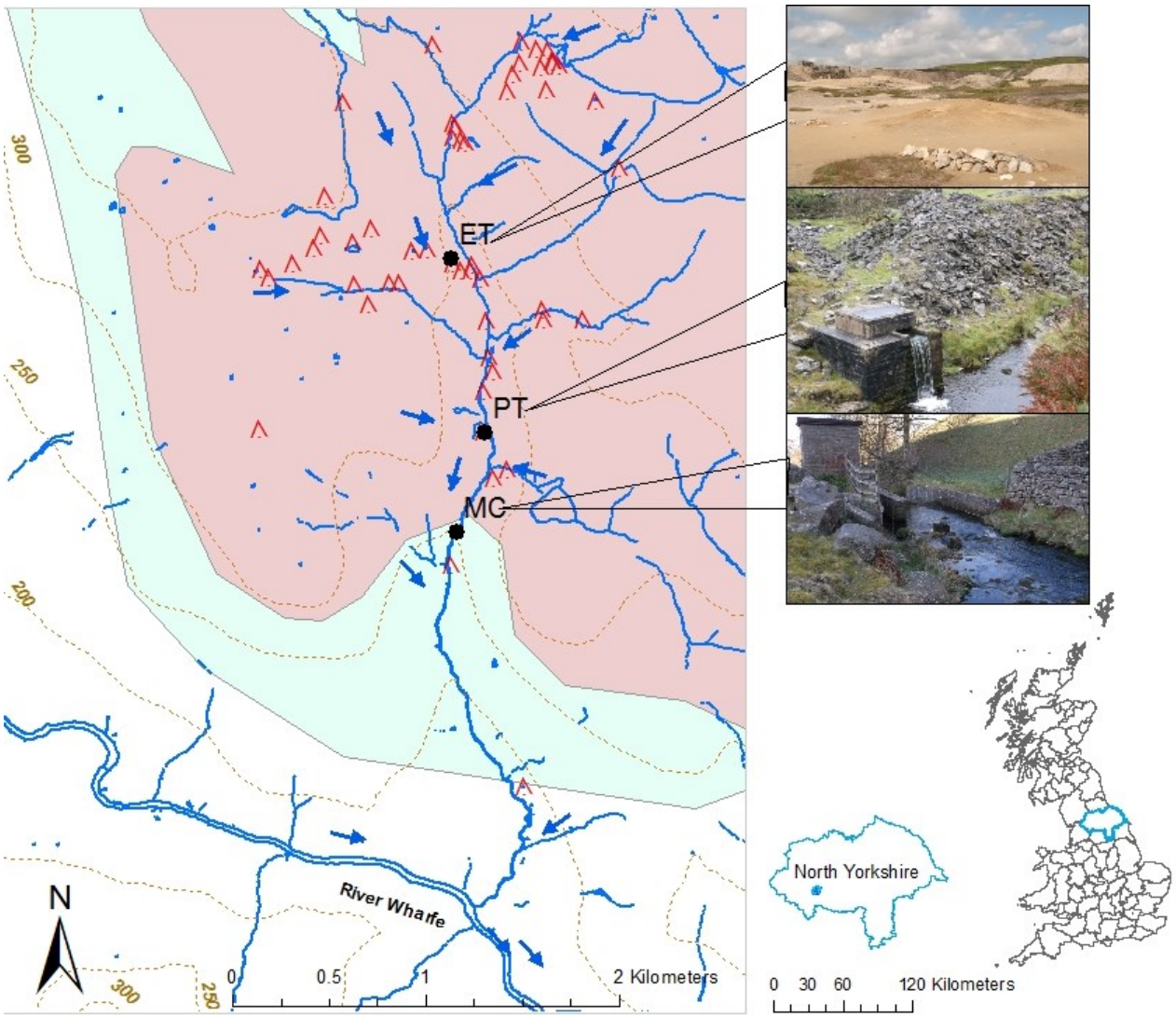
Appendix 3. 7. Percentages of macroinvertebrate families from the Order Trichoptera (caddisfly).



Appendix 3. 8. Percentages of macroinvertebrate families from the Order Plecoptera (stonefly).

Appendices-Chapter 4

Methods-Study area



Legend

- Sampling sites
- Mine structures (e.g. dressing floors, adits, shafts, smelt mills)
- Waterways
- Elevation (m)

Geology-Bedrock

- Millstone grit (mudstone, siltstone, sandstone)
- Liddesdale-Yoredale (limestone, sandstone, siltstone, mudstone)

Appendix 4. 1. Sampling sites at Hebden Beck showing the underlying geology comprised by the Millstone grit and Liddesdale-Yoredale bedrock. Hydrological and Geological base maps contain OS data © Crown copyright and database right (2016).

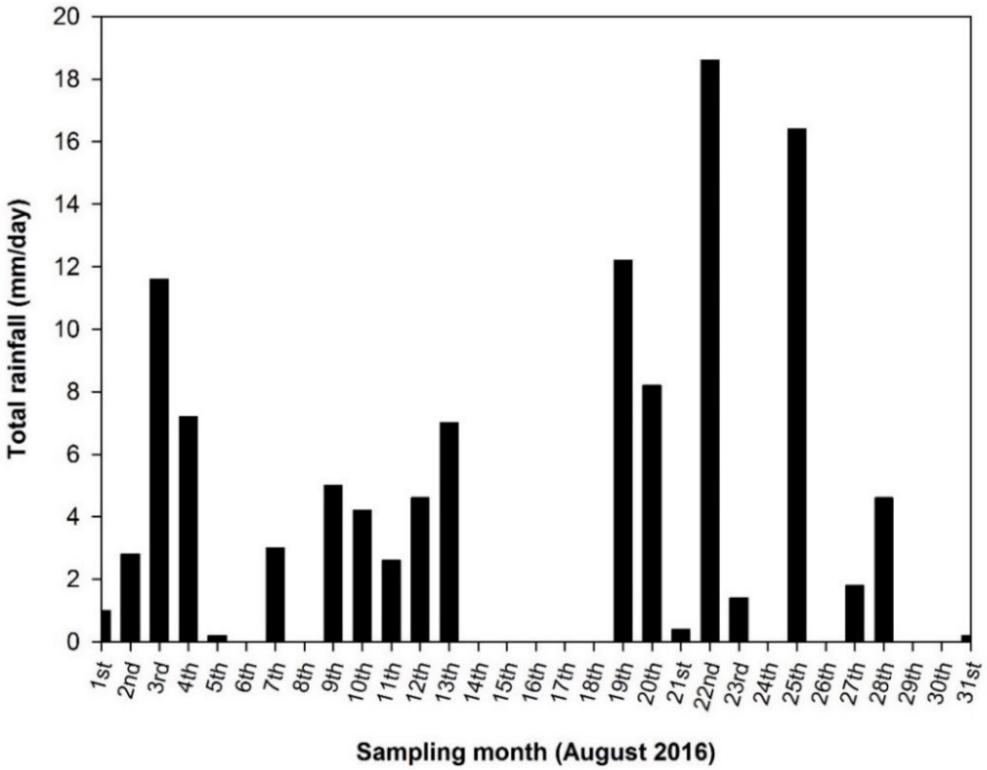
Appendix 4. 2. Sampling sites along Hebden Beck. Three locations were adopted from Valencia-Avellan et al. (2017).Table indicates site elevation, coordinates, and distance from River Wharfe. Sites are listed from upstream to downstream.

Sites ID	Sites ID from Valencia-Avellan et al. (2017)	Sites description	Elev. (m)	Coordinates		From R. Wharfe (m)
				East	North	
ET	H12	Ephemeral tributary running through Beaver spoil wastes (Yarnbury mine)	285	402451	465822	3921
PT	H5	Perennial tributary flowing through mine channels (Duke's adit)	256	402638	464793	2836
MC	H2(*)	Main river channel	235	402488	464275	2271

(*) Gauging station (F1960) from the UK-Environment Agency.

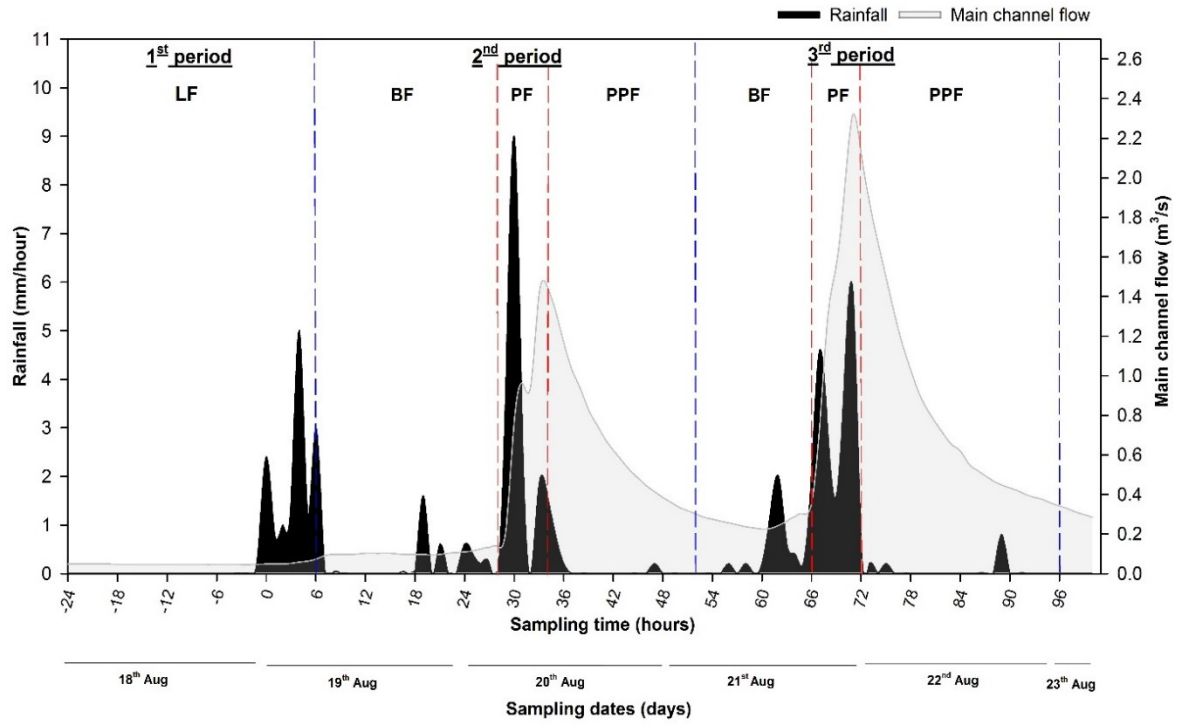
Methods: Characterization of local seasonal conditions and episodic rainfall for August 2016.

Daily rainfall data were obtained for Pateley Bridge Ravens Nest (54°04'01.2"N 1°46'01.2"W) in order to present local seasonal drought and rainfall events for the month of August 2016 (> 12 mm during high rainfall days).



Appendix 4. 3. Daily rainfall records from Pateley Bridge Ravens Nest (54°04'01.2"N 1°46'01.2"W) during August 2016.

Three rainfall events (≥ 5 mm/hour) occurred during the sampling campaigns (Appendix 4.4). A low flow period (LF: 0.05 m^3/s) was measured for 0-6 hours. The first rainfall episode (5 mm/hour) produced little change in flow (0.07 m^3/s), insufficient to identify flow stages. Subsequent episodes (>5 mm/hour) allowed the characterisation of three stages; base flow (BF), peak flow (PF) and post peak flow (PPF). The second event (9 mm/hour), BF corresponded to 7-28 hours, with flow values ranging from 0.07 to 0.14 m^3/s, PF corresponded to 29-34 hours, with flow ranging from 0.22 to 1.45 m^3/s, and PPF was between 35-52 hours, with flow ranging from 1.33 to 0.30 m^3/s. In the third event (5.8 mm/hour), unexpected problems (sampler malfunctioned or swept-away) restricted the sampling duration in sites PT and MC. During this last event, flow stages were characterised as BF from 54-66 hours (flow 0.23 to 0.40 m^3/s), PF from 68-72 hours (flow 1.41 to 2.12 m^3/s), and PPF from 74-96 hours (flow 1.64 to 0.34 m^3/s).



Appendix 4. 4. Hourly rainfall (mm) at Grimwith reservoir (station code: 62046; 54°04'16.4"N 1°54'47.7"W) and main channel flow at gauging station-F1960 (54°04'27.8"N 1°57'48.5"W) from 18th to 23nd of August.

Methods: Distribution of metal chemical species

Measurements of temperature and dissolved water chemistry were used as input data in the Windermere Humic Aqueous Model (WHAM/Model VII). Concentrations of dissolved organic carbon were converted to fulvic acid assuming DOM to be

composed of 50% carbon and the active fraction considered to be 65% fulvic acid (FA= DOC x 1.3) (Tipping et al., 2008). We considered the presence of oxides as being either active or inactive with respect to surface sorption as described in Valencia-Avellan et al., (2018). Activity of Al and Fe oxides was calculated from the dissolved metal data and the equations derived by Tipping (2005), and Lofts and Tipping (2011) respectively, with the lower of the two values being adopted, in order to exclude the likelihood of colloidal material being included in the dissolved fraction.

Results: Concentrations of major anions

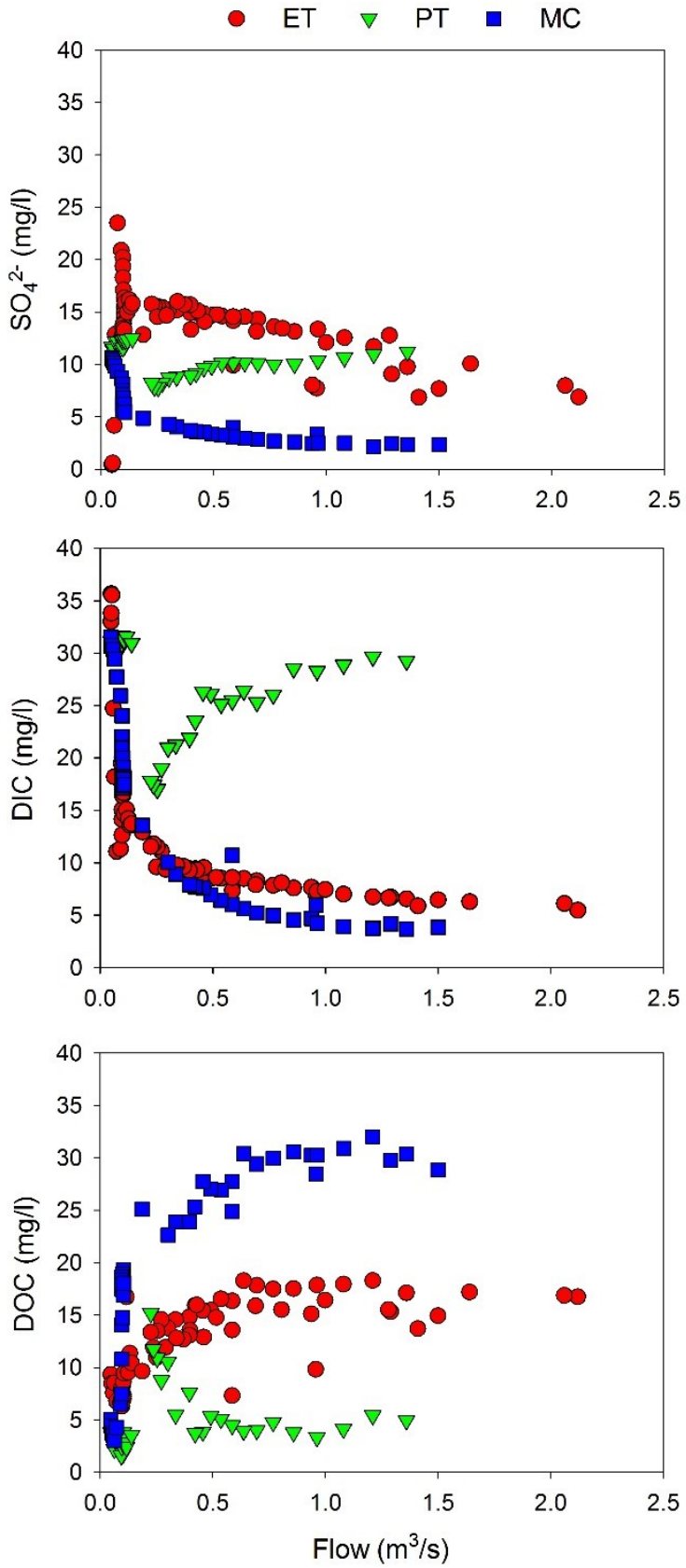
Different concentrations were measured for SO_4^{2-}, DIC and DOC possible due to overland flow or interflow have been identified. From LF to PPF, a 2300% increase in SO_4^{2-} concentrations occurred in ET, which are likely to be related to the degree of erosion and oxidation of mine wastes. In MC, a significant increase (6960%) was observed for DOC concentrations as result of overland flow running through peat moorland areas (Tranvik and Jansson, 2002) while DIC concentrations decreased (212%) due to interflow, attenuating rich-limestone groundwater (Jarvie et al., 1997) (Appendices 4.1 and 4.2). Ranges of SO_4^{2-} and DIC concentrations were higher in ET (0.4 to 23.5 mg/l SO_4^{2-}, 5.5 to 35.7 mg/l DIC) and PT (7.8 to 12.5 mg/l SO_4^{2-}, 17.0 to 31.7 mg/l DIC), while DOC concentrations showed the greatest variation in MC (3.0 to 32.0 mg/l) (Appendix 4.5).

Appendix 4. 5. Water quality parameters and metal concentrations at different flow stages in ephemeral tributaries (ET), perennial tributaries (PT) and main channel (MC).

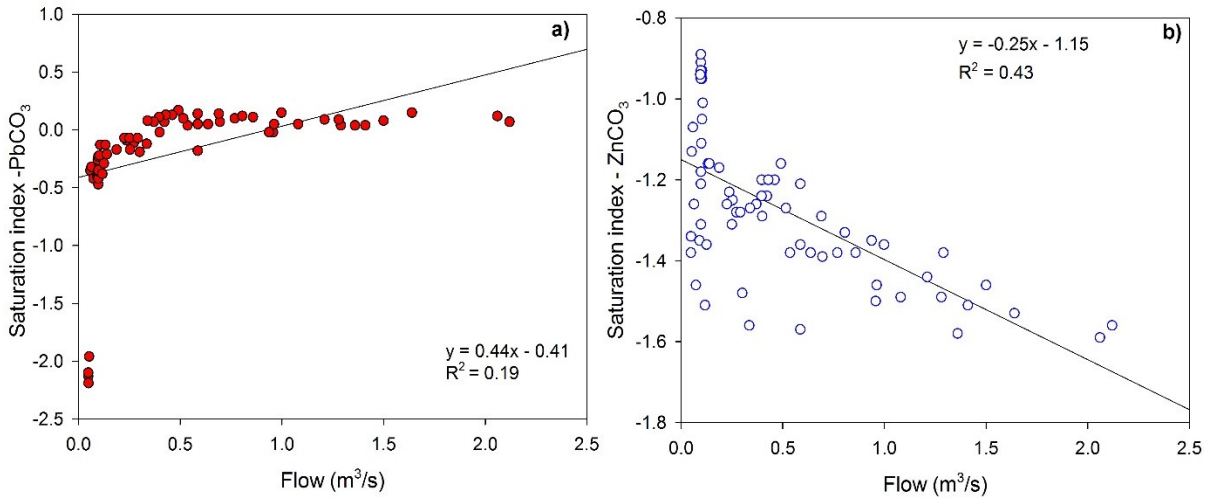
Sites	Rainfall periods	Flow stages		pH	SO_4^{2-} mg/l	DIC mg/l	DOC mg/l	Pb µg/l	Zn µg/l	Fe µg/l	Al µg/l
ET	1st period	LF	Ave	7.2	6.1	27.4	8.5	55.1	2973.7	469.7	9.8
	(5mm/hour)		Max	7.6	23.5	35.7	9.3	128.2	3578.3	2154.5	23.3
			Min	7.0	0.4	11.1	6.8	2.2	1728.5	138.7	1.8
		BF	Ave	7.5	15.6	16.4	8.4	150.4	3298.9	331.2	36.9
			Max	7.7	20.9	20.0	16.7	233.5	3823.0	500.5	54.4
			Min	7.2	12.7	11.3	6.3	106.5	2461.1	167.7	25.3
	2nd period	PF	Ave	7.6	9.2	8.0	12.0	335.3	2414.0	192.6	66.8
			Max	7.6	12.9	12.9	15.3	457.3	2883.9	234.9	106.2
	(9mm/hour)		Min	7.6	7.7	6.4	7.3	206.7	1708.0	158.2	26.3
		PPF	Ave	7.4	13.9	8.3	16.6	467.7	3819.3	245.7	126.5
			Max	7.5	15.2	9.7	18.3	559.1	5016.8	309.0	160.7
			Min	7.2	9.8	6.5	13.8	323.6	3013.0	206.1	70.5
		BF	Ave	7.3	15.0	10.6	12.8	342.7	3807.5	263.7	66.1
			Max	7.4	15.8	11.8	14.6	394.8	4166.9	327.8	77.1
			Min	7.3	13.3	9.4	10.9	284.9	3332.4	221.9	54.8
	3rd period	PF	Ave	7.5	7.2	5.8	15.8	571.8	2538.1	190.3	131.1
			Max	7.5	8.0	6.1	16.9	649.2	2616.5	196.4	163.3
	(5.8mm/hour)		Min	7.4	6.9	5.5	13.7	499.9	2437.2	187.1	98.3
		PPF	Ave	7.4	14.0	8.4	14.7	575.6	3884.9	264.9	125.4
			Max	7.4	16.0	9.7	17.2	690.3	4687.8	309.3	147.2
			Min	7.4	10.1	6.3	12.7	479.1	2914.5	189.7	99.4
PT	1st period	LF	Ave	7.4	11.8	30.9	3.1	50.3	988.4	75.4	42.6
	(5mm/hour)		Max	7.4	12.2	31.1	3.8	63.6	1069.1	80.0	45.6
			Min	7.3	11.5	30.6	2.2	39.9	933.1	70.6	37.4
		BF	Ave	7.5	12.3	31.2	2.7	36.3	932.1	65.4	32.6
			Max	7.6	12.5	31.7	3.8	63.6	1069.1	80.0	57.3
			Min	7.4	11.6	30.8	1.6	31.2	868.2	58.9	27.4
	2nd period	PF	Ave	7.5	11.3	28.4	5.1	30.9	789.0	79.8	42.6
	(9mm/hour)		Max	7.6	12.1	30.8	7.6	35.6	918.2	98.5	52.0
			Min	7.5	10.4	25.6	3.0	23.2	622.8	60.3	28.7
		PPF	Ave	7.4	9.5	24.0	6.3	87.6	659.4	110.6	91.6
			Max	7.5	11.2	29.7	15.1	211.7	771.7	178.6	159.2
			Min	7.3	7.8	17.0	3.3	33.2	567.2	71.0	41.6
MC	1st period	LF	Ave	8.1	10.2	30.1	4.0	27.6	467.4	164.3	39.7
	(5mm/hour)		Max	8.1	10.7	31.5	5.0	38.5	495.5	253.6	51.2
			Min	7.8	9.4	27.7	3.0	23.3	449.5	129.3	34.1
		BF	Ave	8.0	6.4	19.2	16.2	71.1	622.8	940.3	104.0
			Max	8.1	8.7	26.0	19.3	79.8	693.6	1168.2	133.9
			Min	8.0	5.5	17.1	6.5	47.4	493.4	362.1	50.6
	2nd period	PF	Ave	7.4	3.3	7.2	27.9	124.9	512.0	1146.1	214.3
	(9mm/hour)		Max	7.6	4.9	13.6	30.2	153.7	574.7	1326.1	250.7
			Min	7.3	2.3	3.8	24.8	110.6	447.2	1052.4	154.9
		PPF	Ave	7.3	3.2	6.4	27.7	127.8	507.1	1136.2	258.2
			Max	7.6	4.3	10.0	32.0	140.7	536.3	1314.3	293.6
			Min	7.2	2.2	3.7	22.6	116.4	489.3	933.1	230.2

Appendix 4. 6. Pearson correlation coefficient showing relationships between flow, water quality parameters and with metal concentrations at different flow stages. NC: no correlation as pH values were constant (standard deviation= 0), ND= no data available.

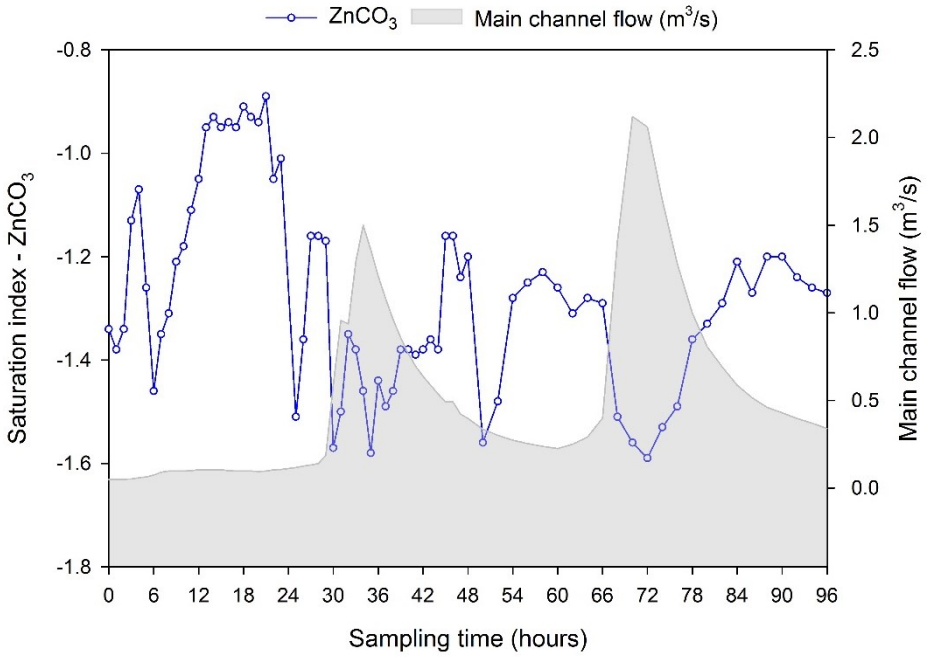
		ET					PT					MC				
		Pb	**Zn**	**Fe**	**Ca**	**Al**	**Pb**	**Zn**	**Fe**	**Ca**	**Al**	**Pb**	**Zn**	**Fe**	**Ca**	**Al**
LF	**pH**	0.9	-0.9	0.3	-0.9	1.0	-0.8	0.4	-0.01	-0.6	-0.4	0.2	0.2	0.3	-0.4	0.2
	flow	0.9	-0.8	0.1	-1.0	0.9	-0.8	0.04	-0.4	-0.8	-0.6	0.9	0.9	1.0	-1.0	0.9
	SO_4^{2-}	0.8	-0.8	-0.1	-1.0	0.9	-0.3	0.2	-0.04	-0.7	-0.2	-0.9	-0.9	-1.0	1.0	-0.9
	DIC	-0.9	0.9	-0.1	1.0	-1.0	0.9	0.4	0.7	0.6	0.8	-1.0	-0.9	-1.0	1.0	-0.9
	DOC	-0.8	0.5	-0.4	0.8	-0.8	0.6	-0.5	-0.2	0.2	-0.1	-0.1	-0.2	-0.1	0.3	-0.3
BF	**pH**	-0.1	0.3	0.4	0.5	0.03	-0.2	-0.03	-0.2	-0.2	-0.1	-0.6	-0.6	-0.6	0.1	-0.8
	flow	0.8	-0.2	-0.03	-0.5	0.7	-0.4	-0.1	-0.3	-0.4	-0.2	0.6	0.3	0.5	-0.3	0.6
	SO_4^{2-}	-0.3	-0.5	-0.9	-0.7	-0.3	0.04	0.2	0.1	-0.2	0.1	-0.8	-0.7	-0.8	0.1	-0.9
	DIC	-0.2	0.7	0.8	1.0	-0.1	0.1	-0.1	0.01	-0.2	0.2	-0.8	-0.7	-0.8	0.2	-1.0
	DOC	0.6	-0.4	-0.01	-0.3	0.5	0.04	-0.02	0.03	-0.2	-0.2	0.8	0.8	0.8	-0.2	0.9
PF	**pH**	NC	NC	NC	NC	NC	-0.3	0.1	-0.4	0.4	-0.6	0.4	0.4	0.9	0.8	-0.8
	flow	1.0	0.3	-0.3	-0.8	0.9	0.01	-0.5	0.8	-0.7	0.9	0.1	-0.6	-0.4	-0.9	0.9
	SO_4^{2-}	-0.8	0.01	0.6	0.9	-0.6	0.3	0.9	-1.0	1.0	-0.9	-0.02	0.6	0.7	1.0	-1.0
	DIC	-0.7	0.2	0.7	1.0	-0.5	0.4	0.9	-1.0	0.9	-0.9	0.1	0.7	0.7	1.0	-1.0
	DOC	0.8	0.8	0.4	-0.3	1.0	-0.4	-0.9	0.9	-1.0	0.9	-0.3	-0.7	-0.8	-0.9	0.9
PPF	**pH**	0.7	0.1	0.04	-0.6	0.6	-0.7	-0.4	-0.7	0.8	-0.8	-0.9	0.2	-1.0	1.0	-0.9
	flow	0.6	-0.5	-0.6	-1.0	0.7	-0.8	0.03	-0.8	0.9	-0.9	0.9	0.3	0.7	-0.9	0.8
	SO_4^{2-}	-0.5	0.6	0.6	0.9	-0.6	-0.9	-0.3	-0.9	1.0	-0.9	-1.0	-0.1	-0.9	1.0	-0.9
	DIC	-0.7	0.4	0.5	1.0	-0.8	-0.9	-0.3	-1.0	1.0	-1.0	-1.0	-0.02	-0.9	1.0	-0.9
	DOC	0.7	-0.3	-0.5	-0.8	0.7	0.9	0.5	0.9	-0.8	0.8	0.9	-0.01	0.9	-1.0	0.8
BF	**pH**	0.8	-0.7	-0.3	-0.7	-0.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	flow	0.7	-0.5	-0.4	-0.7	0.4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	SO_4^{2-}	-0.7	0.8	0.6	0.9	-0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	DIC	-0.7	0.9	0.7	1.0	-0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	DOC	-0.1	0.4	0.4	0.3	0.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PF	**pH**	-0.6	-1.0	0.04	-1.0	-0.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	flow	0.8	-0.3	-1.0	0.3	0.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	SO_4^{2-}	0.9	0.7	-0.5	1.0	0.9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	DIC	0.4	1.0	0.2	0.9	0.4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	DOC	0.9	-0.2	-1.0	0.4	0.9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PPF	**pH**	-0.6	-0.4	0.2	0.4	-0.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	flow	0.8	-0.7	-0.9	-1.0	0.7	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	SO_4^{2-}	-0.9	0.6	0.9	1.0	-0.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	DIC	-0.9	0.6	0.9	1.0	-0.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	DOC	0.8	-0.4	-0.7	-0.8	0.7	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND



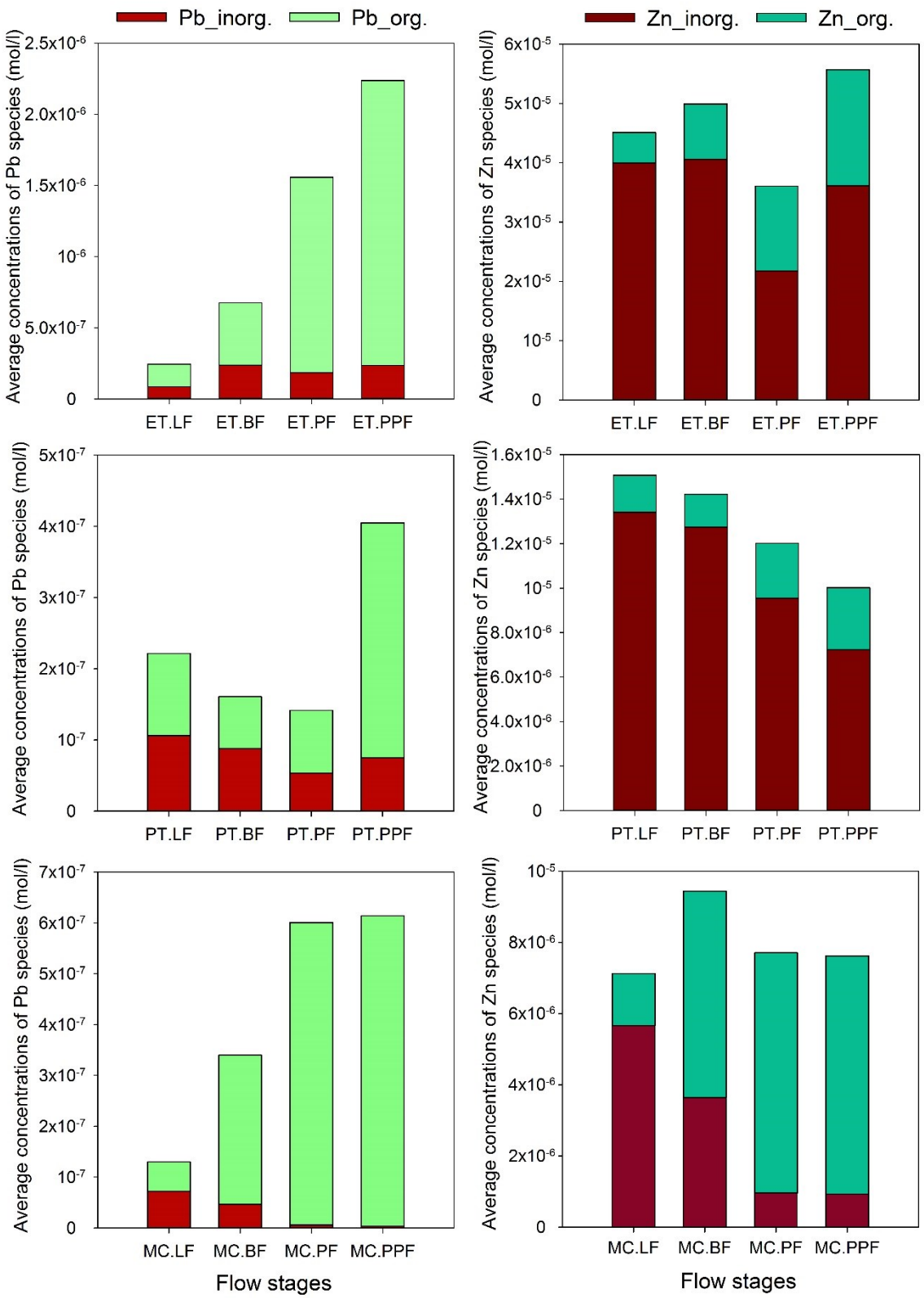
Appendix 4. 7. Effects of episodic flow in concentrations of SO_4^{2-}, DIC and DOC in the three sampling sites.



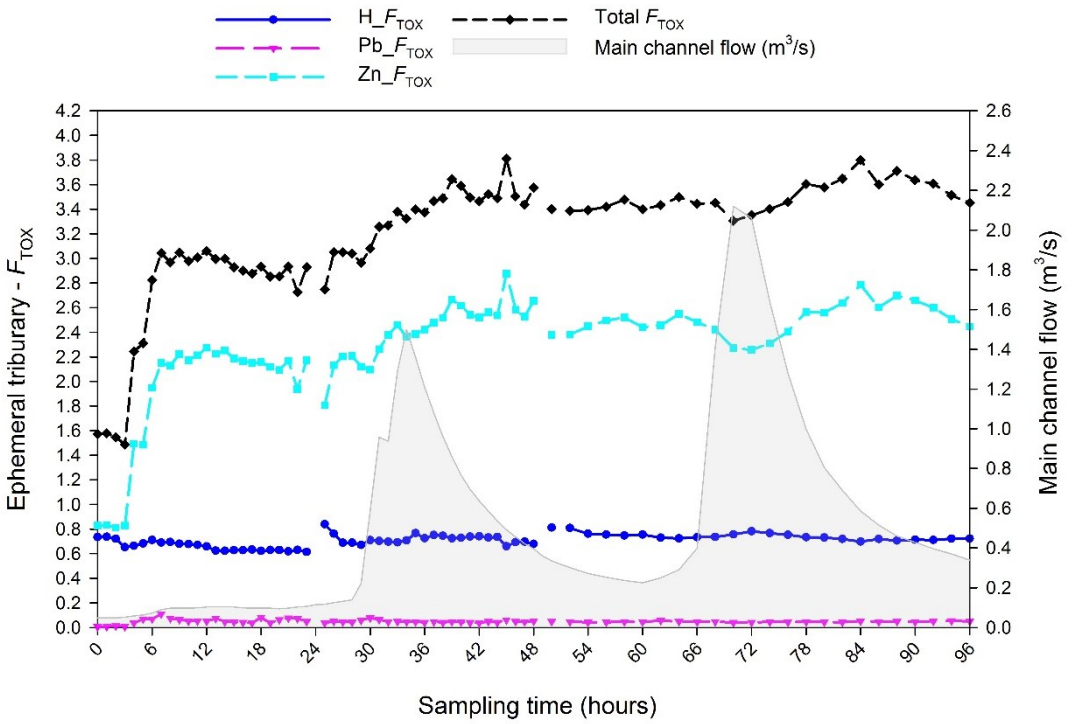
Appendix 4. 8. Relationships between saturation indexes for cerussite ($PbCO_3$) and smithsonite ($ZnCO_3$) with episodic flow in ET. Indexes were computed with PHREEQC model. Note Y axis have different scales.



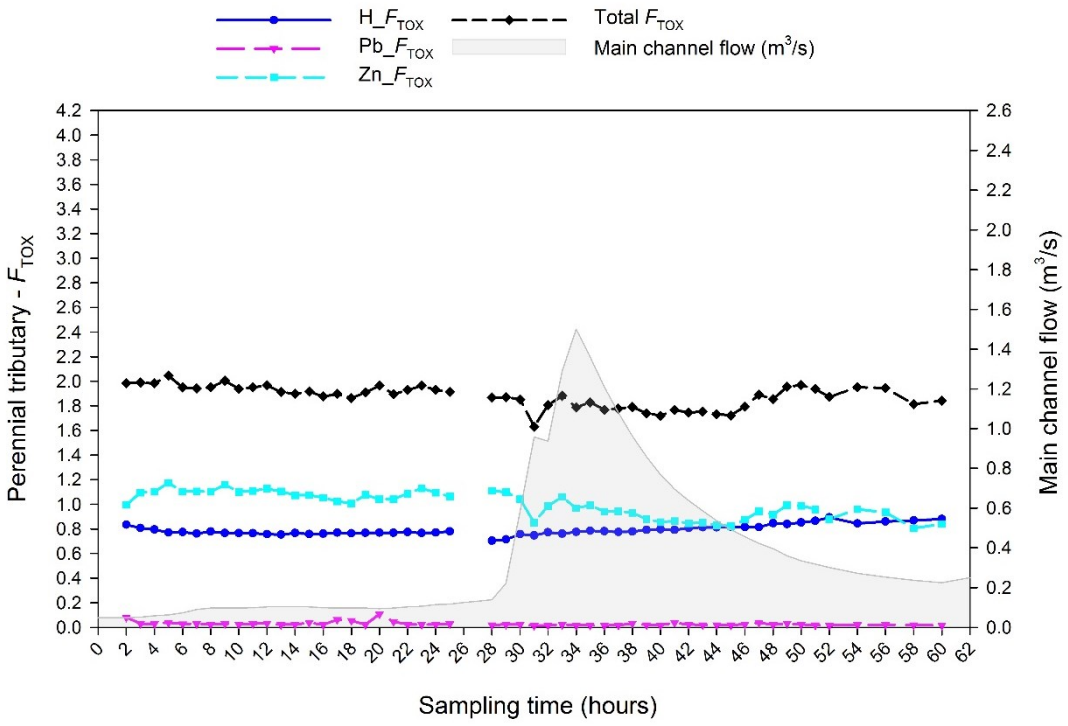
Appendix 4. 9. Effect of peak flow in the kinetics of smithsonite ($ZnCO_3$).



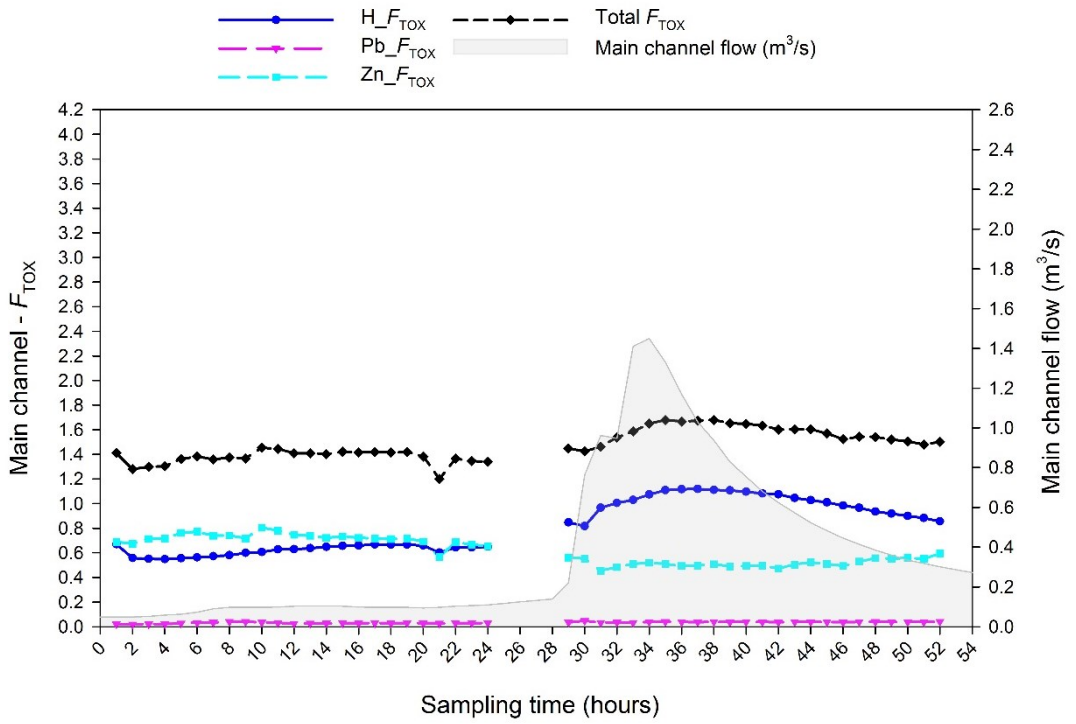
Appendix 4. 10. Inorganic and organic metal concentrations in absence of active oxide precipitates calculated by WHAM/Model VII at different flow stages in all sampling sites. Left hand side panels show average concentrations of Pb species. Right hand side panels show average concentrations of Zn species.



Appendix 4. 11. Variations in F_{TOX} in ephemeral tributary at different flow stages.



Appendix 4. 12. Variations in F_{TOX} in perennial tributary at different flow stages.



Appendix 4. 13. Variations in F_{TOX} in main channel at different flow stages.

Appendices-Chapter 5

Appendix 5. 1. Ethical approval for residents and visitors survey.

Performance, Governance and Operations
Research & Innovation Service
Charles Thackrah Building
101 Clarendon Road
Leeds LS2 9LJ Tel: 0113 343 4873
Email: ResearchEthics@leeds.ac.uk

UNIVERSITY OF LEEDS

Magaly Valencia Avellan
School of Geography
University of Leeds
Leeds, LS2 9JT

ESSL, Environment and LUBS (AREA) Faculty Research Ethics Committee
University of Leeds

Dear Magaly
Title of study: **Assessing public perceptions of river water quality**
Ethics reference: **LTGEOG-024**

I am pleased to inform you that the above research application has been reviewed by a representative of the ESSL, Environment and LUBS (AREA) Faculty Research Ethics Committee and I can confirm a favourable ethical opinion as of the date of this letter. The following documentation was considered:

Document	Version	Date
LTGEOG-024 LightTouchEthicsForm_MValencia.doc	1	01/04/16
LTGEOG-024 Information sheet for residents_v2.0.doc	1	01/04/16
LTGEOG-024 Information Sheet for Tourists v2.0.docx	1	01/04/16
LTGEOG-024 Questionnaires v2.0.xlsx	1	01/04/16

Please notify the committee if you intend to make any amendments to the original research as submitted at date of this approval, including changes to recruitment methodology. All changes must receive ethical approval prior to implementation. The amendment form is available at http://ris.leeds.ac.uk/EthicsAmendment.

Please note: You are expected to keep a record of all your approved documentation, as well as documents such as sample consent forms, and other documents relating to the study. This should be kept in your study file, which should be readily available for audit purposes. You will be given a two week notice period if your project is to be audited. There is a checklist listing examples of documents to be kept which is available at http://ris.leeds.ac.uk/EthicsAudits.

We welcome feedback on your experience of the ethical review process and suggestions for improvement. Please email any comments to ResearchEthics@leeds.ac.uk.
Yours sincerely
Jennifer Blaikie
Senior Research Ethics Administrator, Research & Innovation Service
On behalf of Dr Andrew Evans, Chair, AREA Faculty Research Ethics Committee
CC: Student's supervisor

Appendix 5. 2. Resident's survey

School of Geography
University of Leeds
Leeds LS2 9JT
0113 343 3373
http://www.geog.leeds.ac.uk/

July 2016

Dear Hebden Resident

We would like to invite you to complete a short questionnaire about Hebden Beck. The questionnaire forms part of a PhD project in the School of Geography at the University of Leeds and seeks to understand how important the beck is to the village and village life. The PhD project is looking at a range of catchment-scale water quality and quantity issues, from water chemistry to flow data, and we would like to find out what you think about these topics as residents of Hebden.

The questionnaire should take around 10 minutes to complete and should be completed by one member of your household: if more people in your household would like to complete a questionnaire, an online version is available (https://leeds.onlinesurveys.ac.uk/hebdenvillage) and additional paper copies can be obtained from The Old School Tea Room.

Your participation is completely voluntary, although you must be 18 years or older to complete this survey. You do not have to answer every question or complete all the survey, but we would greatly benefit from your full participation. Once we have collected the survey, you will not be contacted again unless you request further contact in the 'Additional Feedback' section of the questionnaire.

The questionnaire is completely anonymous and we will not ask for any personal data which will identify you. Furthermore, individual responses will remain confidential and only accessible to the research team named below. Once the data from each questionnaire has been extracted into a database, each questionnaire will be destroyed. The aim is to create a short report describing the combined data which will be available in the public domain and will be shared with local authorities, conservation bodies and other organisations with responsibility for rivers so offers you the opportunity to comment on the Beck and any changes you feel could improve the village and other areas associated with the river system.

If you are happy to take part, please complete the consent clause below before turning the page to start the survey. If you have queries about this work please contact the research team: Magaly Valencia (gymgv@leeds.ac.uk) or Rebecca Slack (r.slack@leeds.ac.uk; 0113 343 3373). We will be visiting Hebden **TOMORROW (Saturday 2nd July)** to collect completed questionnaires so if you are unlikely to be in, please leave your completed questionnaire on your doorstep or other visible/accessible place in the clear plastic bag provided. If we miss you, you can take your completed questionnaire to The Old School Tea Room on Main Street.

Consent clause

Please tick these boxes to confirm that:

- You have read and understood the information above. ☐
- You are willing to contribute to this research. ☐

We hope you enjoy completing the questionnaire, and thank you very much for your participation.

Yours faithfully,

Magaly and Rebecca

UNIVERSITY OF LEEDS

School of Geography
University of Leeds
Leeds LS2 9JT
0113 343 3373

If you complete the online version of this questionnaire instead, please tick this box and place the questionnaire on your doorstep for collection tomorrow (Saturday 2nd July).

Hebden Beck and You

Please take a few minutes to fill out this survey. We welcome your feedback and your answers will be kept confidential. Thank you for your participation.

Water levels

1. Have you personally been affected by the flooding of last winter? This might be at home, at work, commuting/travelling etc. Please tick.

☐ Yes ☑ No

2. Have you ever experienced flooding of Hebden Beck? Please tick and expand if required.

☐ Yes. Please provide approx. location:
☐ No – not of Hebden Beck but of other local rivers. Please state:
☐ No – no experience

3. Do you think water levels in Hebden Beck are increasing generally?

☐ Yes ☐ No ☐ Note sure/Don't know

Hebden village

4. How important are the following to the village? Please tick.

	Agree strongly	Agree slightly	Neither agree nor disagree	Disagree slightly	Disagree strongly
Tourists and visitors	☐	☐	☐	☐	☐
Farming and fisheries	☐	☐	☐	☐	☐
Other local businesses	☐	☐	☐	☐	☐
Commuting distance to other towns/cities	☐	☐	☐	☐	☐
Varied community structure	☐	☐	☐	☐	☐
Other (please specify):	☐	☐	☐	☐	☐

5. What do you like about Hebden? Please tick.

	Like strongly	Like slightly	Neither like nor dislike	Dislike slightly	Dislike strongly
Landscape and wildlife	☐	☐	☐	☐	☐
Community and local facilities	☐	☐	☐	☐	☐
Location in National Park	☐	☐	☐	☐	☐
Accessibility to towns/cities	☐	☐	☐	☐	☐
Archaeology and history	☐	☐	☐	☐	☐
Walking and leisure pursuits	☐	☐	☐	☐	☐
Attractiveness to visitors	☐	☐	☐	☐	☐
Other (please specify):	☐	☐	☐	☐	☐

6. How important is Hebden Beck to the village of Hebden? Please tick.

	Extremely important	Very important	Neither important nor unimportant	Not very important	Unimportant
Provides a wildlife habitat	☐	☐	☐	☐	☐
Provides an attractive focus for the village	☐	☐	☐	☐	☐
Supports farming & fisheries	☐	☐	☐	☐	☐
Supports other business sectors	☐	☐	☐	☐	☐
Source of drinking water	☐	☐	☐	☐	☐
Attracts visitors to the village	☐	☐	☐	☐	☐
Other (please specify):	☐	☐	☐	☐	☐

Hebden Beck

7. How would you rate the water quality in Hebden Beck? Please tick.

☐ Very good ☐ Good ☐ Average ☐ Poor ☐ Bad ☐ Don't know

8. Do you think that the water quality in Hebden Beck should be improved? Please tick.

☐ Yes ☐ No ☐ Don't know

9. Are you aware of national water quality standards for rivers/streams? Please tick.

☐ Yes ☐ No ☐ Don't know

10. Do you know who has responsibility for assessing the water quality of Hebden Beck? Please tick.

☐ Yorkshire Water ☐ Environment Agency ☐ National Park Authority
☐ Craven Council ☐ Other. Please state:

11. Have you ever contacted anyone/any organisation with regard to Hebden Beck? Please tick.

☐ Yes. Please state:
☐ No

Beyond the village

12. Are you aware of the lead mines around Hebden and their part in the local history of the area? Please tick.

☐ Yes – I am aware of the mines and they are an important part of the cultural legacy and landscape.
☐ Yes – I am aware of the mines and they are an unfortunate legacy that detract from the landscape.
☐ Yes – I am aware of the mines but don't know much about them/have not considered them before.
☐ No – I had not heard about the mines before.

13. Do you think the mines have had any effect on the water quality of Hebden Beck? Please tick one.

☐ Yes – but only in the past ☐ Yes – but only now ☐ Yes – now and in the past
☐ Not really thought about it before but suppose they do ☐ Yes but only if it rains heavily
☐ Don't know ☐ No

14. Please tick the box which best corresponds to your opinion for each of the statements below.

	Agree	Disagree	Don't know
The mines discolour the water in Hebden Beck	☐	☐	☐
The moorland above the village discolours the water in Hebden Beck	☐	☐	☐
The mines discharge heavy metals into Hebden Beck	☐	☐	☐
Water from the mines only enters Hebden Beck after heavy rainfall	☐	☐	☐
Farming activities are affected by the mines	☐	☐	☐

Improving Hebden Beck

15. If there was an issue with Hebden Beck (either linked to poor water quality or increased flood potential), would you support interventions to improve the situation? Please tick all that apply.

☐ Yes - if there was a flooding risk ☐ Yes – to improve water quality ☐ No ☐ Don't know

16. If a continuing water quality problem was identified, would you support any of the following remediation/treatment interventions? Please tick all that apply.

☐ Creation of artificial wetlands ☐ Creation of limestone ponds ☐ Use of water treatment plant*

☐ None of the above –continue as is now ☐ Don't know

☐ Other – please state:

*Water treatment plant usually seen at sewage treatment works e.g. settlement tanks, activated sludge etc.

About you

17. As the person completing this questionnaire, please indicate your age range and gender.

☐ 18-30 ☐ 31-43 ☐ 44-56 ☐ 57-69 ☐ >70

☐ Male ☐ Female ☐ Other

18. How many adults and children live in your household? Please write a number.

Adults (>18 years): Children (<18 years):

19. How would you describe the working status of your household? Please tick all that apply.

☐ Retired ☐ Work in Hebden ☐ Work locally (<10miles) ☐ Commute to work (>10 miles)
☐ Not working ☐ Student ☐ Other:

20. How long has your household lived in Hebden? Please tick one.

☐ Less than 5 years ☐ 5-10 years ☐ 10-20 years ☐ More than 20 years ☐ Visitor

Additional Feedback

Please comment.

Thank you for taking the time to complete this questionnaire. We will be collecting completed questionnaires on **Saturday 2nd July, 10am-12pm**. If you would prefer not to be disturbed, please leave on your doorstep in the bag provided or take to The Old School Tea Room.

Appendix 5. 3. Visitor's survey

School of Geography
University of Leeds
Leeds LS2 9JT
0113 343 3373
http://www.geog.leeds.ac.uk/

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Perceptions of Hebden Beck

What is this about?

We would like to invite you to complete a short questionnaire about Hebden Beck. The questionnaire forms part of a PhD project in the School of Geography at the University of Leeds and seeks to understand how important the beck is to both the village and those who visit the village. The PhD project is looking at a range of catchment-scale water quality and quantity issues, from water chemistry to flow data, and we would like to find out what you think about these issues as visitors to Hebden.

Who is involved in this project?

The research team from the University of Leeds consists of Magaly Valencia (PhD student: gymgv@leeds.ac.uk) and her supervisor Dr Rebecca Slack (r.slack@leeds.ac.uk; 0113 343 3373). They will be responsible for collecting, analysing, and reporting the results. The project has support from the Yorkshire Dales National Park Authority, Environment Agency and Yorkshire Dales Rivers Trust.

How will the questionnaire be used?The questionnaire should take no more than 10 minutes to complete, is completely anonymous and we will not ask for any personal data which will identify you. Your responses will remain confidential and once the data from each questionnaire has been extracted into a database, each questionnaire will be destroyed. The data will be used to prepare a short research report which will be publically available.

Why is the questionnaire important?

We can analyse environmental data about the river water e.g. water chemistry, flow, etc., but it is equally important to understand how important the river is to people who live in Hebden and who visit the village. We want to find out what is important to you as this will help to inform how the beck is managed or how matters relating to the beck are better communicated.

How can you contribute to the success of this project?

If you are 18 years or over and would like to participate, please do complete the questionnaire. You do not have to answer every question and you can withdraw at any time, but we would greatly benefit from your full participation. If you do not have the time to complete it now, you can complete it online: https://leeds.onlinesurveys.ac.uk/hebdenvisit. The success of this project truly depends on your contribution so thank you very much for your time – and interest. If you would like access to the short report, please do visit www.wateratleeds.org later this year.

For more information, please contact us:

Magaly Valencia
PhD student at University of Leeds
gymgv@leeds.ac.uk

Dr Rebecca Slack
water@leeds Coordinator
0113 3433373
r.slack@leeds.ac.uk

Please tick here that you are happy to proceed with the questionnaire on the basis of the information provided above ☐

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School of Geography
University of Leeds
Leeds LS2 9JT
0113 343 3373

Hebden Beck and You

Please take a few minutes to fill out this survey: by completing the survey, you are indicating your consent to participate in this research. We welcome your feedback and your answers will be kept anonymous and confidential. Thank you for your participation.

Interview code: Date/time: Location:

Water levels

1. Have you personally been affected by the flooding of last winter? This might be at home, at work, commuting/travelling etc. Please tick.

☐ Yes ☐ No

2. Have recent national flood events made you more aware of rivers?

☐ Yes ☐ No ☐ Don't know

3. Do you think flooding is generally becoming more frequent?

☐ Yes ☐ No ☐ Note sure/Don't know

Hebden village and environs

4. Why are you visiting Hebden (and/or Hebden environs) today? Please tick.

	Agree strongly	Agree slightly	Neither agree nor disagree	Disagree slightly	Disagree strongly
Ease of access from where I live	☐	☐	☐	☐	☐
Good walking routes	☐	☐	☐	☐	☐
Local facilities e.g. pub/tea shop	☐	☐	☐	☐	☐
Wildlife and landscape	☐	☐	☐	☐	☐
Archaeology and history	☐	☐	☐	☐	☐
Location in the National Park	☐	☐	☐	☐	☐
Other (please specify):	☐	☐	☐	☐	☐

5. Do you think Hebden Beck is important to the village? Please tick.

☐ Yes ☐ No ☐ Note sure/Don't know

6. If YES to Q5, why do you think Hebden Beck is important to the village? Please tick.

	Extremely important	Very important	Neither important nor unimportant	Not very important	Unimportant
Provides a wildlife habitat	☐	☐	☐	☐	☐
Provides an attractive focus for the village	☐	☐	☐	☐	☐
Supports farming & fisheries	☐	☐	☐	☐	☐
Supports other business sectors	☐	☐	☐	☐	☐
Source of drinking water	☐	☐	☐	☐	☐
Attracts visitors to the village	☐	☑	☐	☐	☐
Other (please specify):	☐	☐	☐	☐	☐

Hebden Beck

7. How would you rate the water quality in Hebden Beck? Please tick.

☐ Very good ☐ Good ☐ Average ☐ Poor ☐ Bad ☐ Don't know

8. Do you think that the water quality in Hebden Beck should be improved? Please tick.

☐ Yes ☐ No ☐ Don't know

9. Are you aware of national water quality standards for rivers/streams? Please tick.

☐ Yes ☐ No ☐ Don't know

10. Do you know who has responsibility for assessing the water quality of Hebden Beck? Please tick.

☐ Yorkshire Water Authority ☐ Environment Agency ☐ National Park

☐ Craven Council ☐ Other. Please state:

Beyond the village

11. Are you aware of the lead mines around Hebden and their part in the local history of the area? Please tick.

☐ Yes – I am aware of the mines and they are an important part of the cultural legacy and landscape.
☐ Yes – I am aware of the mines and they are an unfortunate legacy that detract from the landscape.
☐ Yes – I am aware of the mines but don't know much about them/have not considered them before.
☐ No – I had not heard about the mines before.

12. Do you think the mines have had any effect on the water quality of Hebden Beck? Please tick one.

☐ Yes – but only in the past ☐ Yes – but only now ☐ Yes – now and in the past
☐ Not really thought about it before but suppose they do ☐ Yes but only if it rains heavily
☐ Don't know ☐ No

13. Please tick the box which best corresponds to your opinion for each of the statements below.

	Agree	Disagree
The mines discolour the water in Hebden Beck	☐	☐
The moorland above the village discolours the water in Hebden Beck	☐	☐
The mines discharge heavy metals into Hebden Beck	☐	☐
Water from the mines only enters Hebden Beck after heavy rainfall	☐	☐
Farming activities are affected by the mines	☐	☐

14. Do you think that recent flooding events can affect the water quality of Hebden Beck? Please tick.

☐ Yes ☐ No ☐ Don't know
Why?

Improving Hebden Beck

15. If there was an issue with Hebden Beck (either linked to poor water quality or increased flood potential), would you support any of the following remediation/treatment interventions? Please tick all that apply.

☐ Creation of artificial wetlands ☐ Creation of limestone ponds ☐ Use of water treatment plant*

☐ None of the above –continue as is now ☐ Don't know

☐ Other – please state:

*Water treatment plant usually seen at sewage treatment works e.g. settlement tanks, activated sludge etc.

About you

16. As the person completing this questionnaire, please indicate your age range and gender. Please tick.

☐ 18-30 ☐ 31-43 ☐ 44-56 ☐ 57-69 ☐ >70

☐ Male ☐ Female ☐ Other

17. Why are you here today?

☐ Work here ☐ Visiting/tourist ☐ Other (please specify):

18. Where do you live? Please state first part of postcode or town:

19. How would you describe your employment status? Pleas tick.

☐ Retired ☐ Private sector ☐ Public sector ☐ Self-employed
☐ Not working ☐ Student ☐ Other:

20. How often do you visit Hebden? Please tick.

☐ At least once a week ☐ More than once a month ☐ About once a month
☐ 2+ times per year ☐ Annually ☐ First visit

Additional Feedback

Please comment.

Thank you for taking the time to complete this survey.

Appendix 5. 4. Ethical approval for stakeholder's survey.

Research and Innovation Service
Level 11, Worsley Building
University of Leeds
Leeds, LS2 9NL Tel: 0113 343 4873
Email: ResearchEthics@leeds.ac.uk

UNIVERSITY OF LEEDS

Magaly Valencia Avellan
School of Geography
10.11, Garstang building
University of Leeds
Leeds, LS2 9JT

ESSL, Environment and LUBS (AREA) Faculty Research Ethics Committee
University of Leeds

Dear Magaly

Title of study: **Assessing public perceptions of river water quality**
Ethics reference: **LTGEOG-028**

I am pleased to inform you that the above research application has been reviewed by a representative of the ESSL, Environment and LUBS (AREA) Faculty Research Ethics Committee I can confirm a favourable ethical opinion as of the date of this letter. The following documentation was considered:

Document	Version	Date
LTGEOG-028 further information.txt	1	13/09/16
LTGEOG-028 12 09 2016 LightTouchEthicsForm_MValencia_expertsurvey_AS.doc	2	13/09/16

Please notify the committee if you intend to make any amendments to the original research as submitted at date of this approval, including changes to recruitment methodology. All changes must receive ethical approval prior to implementation. The amendment form is available at http://ris.leeds.ac.uk/EthicsAmendment.

Please note: You are expected to keep a record of all your approved documentation, as well as documents such as sample consent forms, and other documents relating to the study. This should be kept in your study file, which should be readily available for audit purposes. You will be given a two week notice period if your project is to be audited. There is a checklist listing examples of documents to be kept which is available at http://ris.leeds.ac.uk/EthicsAudits.

We welcome feedback on your experience of the ethical review process and suggestions for improvement. Please email any comments to ResearchEthics@leeds.ac.uk.

Yours sincerely

Jennifer Blaikie
Senior Research Ethics Administrator, Research & Innovation Service
On behalf of Dr Kahryn Hughes, Chair, AREA Faculty Research Ethics Committee

CC: Student's supervisor(s)

Appendix 5. 5. Stakeholder's survey.

Dear <organisation/institution/company>

I am a PhD student at the School of Geography, University of Leeds and I'm completing a project looking at a range of water quality and quantity variables at catchment-scale, from water chemistry to flood events. As part of this project, I am looking at opinions to rivers in North Yorkshire, particularly focusing on my test catchment of Hebden Beck near Grassington. To this end, I have created a number of questionnaires which have been distributed to residents of the village of Hebden as well as visitors to the area – the response rate has been fantastic! I am also keen to obtain the opinions of people and organisations whose interest in the area, or more generally around rivers and the aquatic environment, might be more specialised or focused. Hence this email to you.

I would like to invite you to take part in a short online survey: https://leeds.onlinesurveys.ac.uk/hebden_stakeholders. The survey, which should take no more than 10-15 minutes to complete, asks a range of questions about your and/or your organisations interest in and opinion of rivers generally but Hebden Beck more specifically. Even if you don't think you know Hebden Beck very well, your feedback will still be very useful to me. Your participation is invaluable for this project; for this reason I hope you can spare a few minutes to complete this survey.

The survey can be completed anonymously but if you would be willing to talk in more detail, please do leave your contact details at the end of the survey to take part in a short telephone interview. Any contact details you provide will not be used for any purpose other than the telephone interview and will be stored separately to the interview responses. All data collected will be kept confidential and used for research purposes only. It is hoped that a research paper will be developed from the outcomes of the survey (combined with responses from residents and visitors) but your identity and that of your organisation will be anonymised.

I would like to take this opportunity of thanking you for taking part in the survey https://leeds.onlinesurveys.ac.uk/hebden_stakeholders and for contributing to my PhD studies. If you have any questions, please do not hesitate to contact me.

Kind regards

Magaly Valencia Avellan
PhD Student

gymgv@leeds.ac.uk
School of Geography, Garstang building
http://www.geog.leeds.ac.uk/people/m.valencia
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School of Geography
University of Leeds
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0113 343 3373

Questionnaire

You are invited to take part in this questionnaire which explores opinions and attitudes to river water quality in North Yorkshire. This survey forms part of a PhD project in the School of Geography at the University of Leeds.

The PhD project is looking at a range of catchment-scale water quality and quantity issues, from water chemistry to flood events. The project has been carried out in a small catchment called Hebden Beck (near Grassington).

Participation in this survey is totally voluntary. All data collected will be kept confidential and used for research purposes only. There are no right or wrong answers in this questionnaire – we only want your opinion. Your name or any identifying characteristics will not be available to anyone, other than my supervisor and me, at any point.

Thank you for your participation, if you have any questions you may contact Magaly Valencia gymgv@leeds.ac.uk (PhD student) or Dr Rebecca Slack r.slack@leeds.ac.uk (Supervisor).

Please tick here that you are happy to proceed with the questionnaire on the basis of the information provided above ☐

Name of organisation:

Completed by:

Date:

About the organisation you work for and your role

1) How would you describe your organisation* and its role?

* Organisation can be a local authority, a government agency, a limited or public limited company, LLP, sole trader, not for profit/third sector etc.

2) Would you describe your organisation as one of the following? Please, tick all that apply.

- □ local
- □ regional
- □ national
- □ global
- □ Others, please specify:

3) What is your role within your organisation? Please describe briefly, including your job title, key tasks and/or role objectives as applicable.

4) How long have you worked for this organisation?

□ <1 year □ ≥1-<3 years □ ≥3-<5 years

□ ≥5-<10 years □ ≥10 years

5) Drawing on your experience in your current role, what do you think are the priority areas for the management of rivers and waterways? Please rank the following options: 1 is most important, 5 or 6 least important.

- □ Protection of water resources.
- □ Protection of aquatic ecosystems.
- □ Abstraction of water.
- □ Improving water quality (surface and groundwater).
- □ Fluvial flood management.
- □ Other (Please specify):

Opinions of Hebden Beck

6) Have you heard of the village of Hebden, near Grassington in North Yorkshire, and its river?

- □ Yes – go to Q7
- □ No – go to Q8

7) If YES to Q6, how important do you think Hebden Beck is to the village of Hebden?

	Extremely important	**Very important**	**Neither important nor unimportant**	**Not very important**	**Unimportant**
Provides a wildlife habitat					
Provides an attractive focus for the village					
Supports farming and fisheries					
Supports other business sectors					
Source of drinking water					
Attracts visitors to the village					

Other (please specify):					

8) Have you ever worked with/on Hebden Beck on issues related to water quality/quantity?

Water Quality

9) Are you familiar with the national water quality standards for rivers/streams?

- ☐ Yes
- ☐ No
- ☐ Don't know

10) If YES to Q9, how would you rate the water quality in Hebden Beck?

☐ Very good ☐ Good ☐ Average ☐ Poor ☐ Bad ☐ Don't know

11) What factors do you think affect the water quality in Hebden Beck?

Mining

12) Are you aware of the historical lead mines around Hebden? Please tick

- ☐ Yes – I am aware of the mines and they are an important part of the cultural legacy and landscape.
- ☐ Yes – I am aware of the mines and they are an unfortunate legacy that detract from the landscape.
- ☐ Yes – I am aware of the mines but don't know much about them/have not considered them before.
- ☐ No - I had no heard about the mines before.

13) Do you think there is an environmental legacy of the lead mines in the area? If yes, please explain why you think this.

- ☐ Yes
- ☐ No
- ☐ Don't know

14) Do you think the mines have or are influencing the water quality of the river? If yes, please explain why you think this.

- ☐ Yes
- ☐ No
- ☐ Don't know

15) Do you think intense rainfall events may alter the influence of mine/mining wastes on the water quality of Hebden Beck? If yes, please explain why you think this.

- ☐ Yes
- ☐ No
- ☐ Don't know

16) Do you think water quality in Hebden Beck can be improved without detracting from landscape/heritage?

- ☐ Yes
- ☐ No
- ☐ Don't know

17) If YES to Q16, would you support any of the following remediation/treatment interventions? Please explain why?

- ☐ Creation of artificial wetlands
- ☐ Creation of limestone ponds
- ☐ Use of water treatment plant*
- ☐ Removal or remediation of spoil heaps?
- ☐ No need (or something similar)
- ☐ Other…

*Water treatment plant usually seen at sewage treatment works e.g. settlement tanks, activated sludge, etc.

Improving river management

18) What aspects of river management should be improved, across England? Please state one opportunity, policy intervention or technique.

19) What can be improved on or around Hebden Beck? Please state one opportunity, policy intervention or technique.

20) What do you think of public engagement as a mechanism for river management? Please tick all that apply.

- ☐ Allows different stakeholders to discuss different needs associated with the river to reach a consensus decision.
- ☐ Permits open and transparent decisions about the river to be made by appropriate organisation.
- ☐ Information can be shared, developed and then integrated into management strategies.
- ☐ Useful to bring river users on-side with difficult decisions.
- ☐ Beneficial to present decisions to river users to reduce later enquiries.
- ☐ A tick-box exercise with limited usefulness.
- ☐ Other reasons, please explain.

21) Are there initiatives related to river management that organisations might be doing/planning (irrespective of community engagement) that might be applicable to Hebden Beck?

Additional Feedback

Would you like to provide any further comment(s) to the issues addressed in this questionnaire?

Is there anyone in your organisation you think we need to speak to about these issues? Please tell us who to contact and provide contact details. We are interested in speaking to individuals in more detail about their opinions of Hebden Beck in particular.

If you would like to have a further discussion about these issues. Please provide your contact details to arrange a telephone interview.

Appendix 5. 6. Selected questions for statistical descriptive analysis.

Analysed questions	Alternative answers and ranks	
Have you personally been affected by the flooding of last winter?	Yes= 1, No= 2, Don't know/ Not answered= 0	
Do you think water levels in Hebden Beck are increasing generally?	Yes= 1, No= 2, Don't know/ Not answered= 0	
Why do you like/visit Hebden?	Residents	Visitors
1. Landscape and wildlife	Like strongly= 1	Agree strongly= 1
2. Community and local facilities	Like slightly= 2	Agree slightly= 2
3. Location in National Park	Neither like nor dislike= 3	Neither agree nor disagree= 3
4. Accessibility to towns/cities	Dislike slightly= 4	Disagree slightly= 4
5. Archaeology and history	Dislike strongly= 5	Disagree strongly= 5
6. Walking and leisure pursuits		
How important is Hebden Beck to the village of Hebden? 1. Provides a wildlife habitat 2. Provides an attractive focus for the village 3. Supports farming & fisheries 4. Supports other business sectors 5. Source of drinking water 6. Attracts visitors to the village	Extremely important= 1, Very important= 2, Neither important or unimportant= 3, Not very important= 4, Unimportant= 5, Don't know/ Not answered= 0	
How would you rate the water quality in Hebden Beck?	Very good= 1, Good= 2, Average= 3, Poor= 4, Bad= 5, Don't know/ Not answered= 0	
Do you think that the water quality in Hebden Beck should be improved?	Yes= 1, No= 2, Don't know/ Not answered= 0	
Are you aware of national water quality standards for rivers/streams?	Yes= 1, No= 2, Don't know/ Not answered= 0	
Are you aware of the lead mines around Hebden and their part in the local history of the area?	Yes-I am aware of the mines and they are an important part of the cultural legacy and landscape= 1, Yes-I am aware of the mines and they are an unfortunate legacy that detract from the landscape= 2, Yes-I am aware of the mines but don't know much about them/have not considered them before= 3, No-I has not heard about the mines before= 4	

Appendix 5.6 (continued). Selected questions for statistical descriptive analysis.

Analysed questions	Alternative answers and ranks
Do you think the mines have had any effect on the water quality of Hebden Beck?	Yes-but only in the past= 1 Yes-but only now= 2 Yes-now and in the past= 3 Yes but only if rains heavily= 4 No really thought about it before but suppose they do= 5 No= 6 Don't know/ Not answered= 0
Please select your opinion for each of the following statements:	Agree= 1 Disagree= 2 Don't know= 0
1. The mines discolour the water in Hebden Beck	
2. The moorland above the village discolours the water in Hebden Beck	
3. The mines discharge heavy metals into Hebden Beck	
4. Water from the mines only enters Hebden Beck after heavy rainfall	
5. Farming activities are affected by the mines	
If a continuing water quality problem was identified, would you support any of the following remediation/treatment interventions?	Creation of artificial wetlands= 1 Creation of limestone ponds= 2 Use of water treatment plant= 3 None of the above-continue as is now= 4 Don't know= 5 Other, please state= 6 Creation of artificial wetlands + Creation of limestone ponds= 7 Creation of artificial wetlands + Creation of limestone ponds + Use of water treatment plant= 8
As the person completing this questionnaire, please indicate your age range:	Male= 1, Female= 2, Other= 3
As the person completing this questionnaire, please indicate your gender:	18-30= 1 31-43= 2 44-56= 3 57-69= 4 >70= 5

Appendix 5.6 (continued). Selected questions for statistical descriptive analysis.

Analysed questions	**Alternative answers and ranks**	
How would you describe the working status of your household?	*Residents*	*Visitors*
	Reitred= 1	Retired= 1
	Work in Hebden= 2	Private sector= 2
	Work locally (<10 miles)= 3	Public sector= 3
	Commute to work (>10 miles)= 4	Self-employed= 4
	Not working= 5	Not working= 5
	Student= 6	Student= 6
	Other= 7	Other= 7
Time in Hebden	*Residents* How long has your household lived in Hebden?	*Visitors* How often do you visit Hebden?
	Less than 5 years= 1 5-10 years= 2 10-20 years= 3 >20 years= 4 Visitor= 5	At least once a week= 1 More than once a month= 2 About once a month= 3 2+ times per year= 4 Annually= 5 First visit= 6

Appendix 5. 7. Outputs from statistical descriptive analysis in SPSS.

Residents	N	Mean	Std. Error of Mean	Median	Mode	Std. Deviation	Variance	Skewness	Std. Error of Skewness	Kurtosis	Std. Error of Kurtosis	Range	Min	Max	Sum
Have you personally been affected by the flooding of last winter?	61	1.8	0.1	1.80[a]	2	0.4	0.2	-0.9	0.3	0.5	0.6	2.0	1	3	110
Do you think water levels in Hebden Beck are increasing generally?	61	2.1	0.1	2.17[a]	2	0.6	0.4	-0.1	0.3	-0.5	0.6	2.0	1	3	131
How important are the following to the village?															
a. Tourists and visitors - Relative importance	61	1.9	0.1	1.69[a]	1	1.1	1.1	1.8	0.3	3.8	0.6	5.0	1	6	114
b. Farming and fisheries - Relative importance	61	1.1	0.1	1.13[a]	1	0.4	0.2	2.8	0.3	7.8	0.6	2.0	1	3	70
c. Other local businesses - Relative importance	61	1.4	0.1	1.25[a]	1	0.8	0.7	3.5	0.3	15.4	0.6	5.0	1	6	83
d. Commuting distance to other towns/cities - Relative importance	61	2.0	0.1	1.86[a]	1	1.0	1.1	1.2	0.3	2.1	0.6	5.0	1	6	122
e. Varied community structure - Relative importance	61	1.8	0.1	1.56[a]	1	1.1	1.2	2.1	0.3	5.5	0.6	5.0	1	6	107
What do you like about Hebden?															
a. Landscape and wildlife	61	1.0	0.0	.[a]	1	0.0	0.0		0.3		0.6	0.0	1	1	61
b. Community and local facilities	61	1.6	0.2	1.39[a]	1	1.3	1.6	2.9	0.3	7.8	0.6	5.0	1	6	99
c. Location in National Park	61	1.8	0.2	1.46[a]	1	1.3	1.6	1.9	0.3	3.2	0.6	5.0	1	6	107
d. Accessibility to towns/cities	61	2.6	0.2	2.40[a]	1	1.5	2.2	0.6	0.3	-0.5	0.6	5.0	1	6	158
e. Archaeology and history	61	1.5	0.1	1.40[a]	1	0.8	0.7	3.0	0.3	13.7	0.6	5.0	1	6	91
f. Walking and leisure pursuits	61	1.4	0.1	1.25[a]	1	1.0	0.9	3.1	0.3	10.6	0.6	5.0	1	6	86
g. Attractiveness to visitors	61	2.4	0.2	2.04[a]	1	1.5	2.3	1.1	0.3	0.5	0.6	5.0	1	6	146

Appendix 5.7 (continued). Outputs from statistical descriptive analysis in SPSS.

Residents	N	Mean	Std. Error of Mean	Median	Mode	Std. Deviation	Variance	Skewness	Std. Error of Skewness	Kurtosis	Std. Error of Kurtosis	Range	Min	Max	Sum
How important is Hebden Beck to the village of Hebden?															
a. Provides a wildlife habitat	61	1.4	0.1	1.34[a]	1	0.5	0.3	1.2	0.3	0.5	0.6	2.0	1	3	83
b. Provides an attractive focus for the village	61	1.7	0.1	1.59[a]	1	1.0	0.9	1.9	0.3	5.7	0.6	5.0	1	6	105
c. Supports farming & fisheries	61	1.5	0.1	1.43[a]	1	0.7	0.5	1.4	0.3	1.8	0.6	3.0	1	4	91
d. Supports other business sectors	61	3.1	0.2	2.94[a]	3	1.5	2.1	0.4	0.3	-0.5	0.6	5.0	1	6	189
e. Source of drinking water	61	3.9	0.2	4.23[a]	5	1.7	2.9	-0.5	0.3	-1.0	0.6	5.0	1	6	235
f. Attracts visitors to the village	61	2.5	0.2	2.36[a]	2	1.2	1.6	0.8	0.3	0.6	0.6	5.0	1	6	152
How would you rate the water quality in Hebden Beck?	61	3.0	0.2	2.50[a]	2	1.8	3.4	0.7	0.3	-0.9	0.6	5.0	1	6	183
Do you think that the water quality in Hebden Beck should be improved?	61	2.3	0.1	2.40[a]	3	0.7	0.5	-0.6	0.3	-0.8	0.6	2.0	1	3	143
Are you aware of national water quality standards for rivers/streams?	61	1.6	0.1	1.52[a]	1	0.7	0.5	0.8	0.3	-0.5	0.6	2.0	1	3	96
Are you aware of the lead mines around Hebden and their part in the local history of the area?	61	1.1	0.1	1.09[a]	1	0.5	0.3	3.3	0.3	9.7	0.6	2.0	1	3	70

Appendix 5.7 (continued). Outputs from statistical descriptive analysis in SPSS.

Residents	N	Mean	Std. Error of Mean	Median	Mode	Std. Deviation	Variance	Skewness	Std. Error of Skewness	Kurtosis	Std. Error of Kurtosis	Range	Min	Max	Sum
Do you think the mines have had any effect on the water quality of Hebden Beck?	61	3.5	0.3	3.09[a]	3	2.2	4.7	0.5	0.3	-1.1	0.6	6.0	1	7	212
Please tick the box which best corresponds to your opinion for each of the statements below.															
a. The mines discolour the water in Hebden Beck	61	2.2	0.1	2.27[a]	2	0.6	0.4	-0.2	0.3	-0.5	0.6	2.0	1	3	137
b. The moorland above the village discolours the water in Hebden Beck	61	1.5	0.1	1.40[a]	1	0.8	0.6	1.1	0.3	-0.4	0.6	2.0	1	3	92
c. The mines discharge heavy metals into Hebden Beck	61	2.3	0.1	2.40[a]	3	0.8	0.7	-0.6	0.3	-1.2	0.6	2.0	1	3	141
d. Water from the mines only enters Hebden Beck after heavy rainfall	61	2.2	0.1	2.27[a]	3	0.8	0.7	-0.4	0.3	-1.5	0.6	2.0	1	3	134
e. Farming activities are affected by the mines	61	2.2	0.1	2.26[a]	2	0.7	0.5	-0.4	0.3	-1.0	0.6	2.0	1	3	135

Appendix 5.7 (continued). Outputs from statistical descriptive analysis in SPSS.

Residents	N	Mean	Std. Error of Mean	Median	Mode	Std. Deviation	Variance	Skewness	Std. Error of Skewness	Kurtosis	Std. Error of Kurtosis	Range	Min	Max	Sum
As the person completing this questionnaire, please indicate your age range:	61	3.8	0.1	3.84[a]	3	1.1	1.3	-0.4	0.3	0.2	0.6	5.0	1	6	233
As the person completing this questionnaire, please indicate your gender:	61	1.8	0.1	1.74[a]	1	0.8	0.6	0.4	0.3	-1.3	0.6	2.0	1	3	110
How would you describe the working status of your household?	61	2.1	0.2	1.73[a]	1	1.6	2.6	1.9	0.3	3.3	0.6	6.0	1	7	131
How long has your household lived in Hebden?	61	3.0	0.1	3.26[a]	4	1.1	1.3	-0.7	0.3	-1.0	0.6	3.0	1	4	184
Visitors	**N**	**Mean**	**Std. Error of Mean**	**Median**	**Mode**	**Std. Deviation**	**Variance**	**Skewness**	**Std. Error of Skewness**	**Kurtosis**	**Std. Error of Kurtosis**	**Range**	**Min**	**Max**	**Sum**
Have you personally been affected by the flooding of last winter?	55	1.8	0.1	1.76[a]	2	0.4	0.2	-1.3	0.3	-0.4	0.6	1.0	1	2	97
Do you think flooding is generally becoming more frequent?	55	1.2	0.1	1.12[a]	1	0.5	0.3	3.1	0.3	8.6	0.6	2.0	1	3	64
4. Why are you visiting Hebden (and/or Hebden environs) today?															
a. Ease of access from where I live	55	2.5	0.2	2.22[a]	1	1.5	2.3	1.0	0.3	0.2	0.6	5.0	1	6	138
b. Good walking routes	55	1.5	0.1	1.23[a]	1	1.1	1.2	3.0	0.3	9.3	0.6	5.0	1	6	80

Appendix 5.7 (continued). Outputs from statistical descriptive analysis in SPSS.

Visitors	N	Mean	Std. Error of Mean	Median	Mode	Std. Deviation	Variance	Skewness	Std. Error of Skewness	Kurtosis	Std. Error of Kurtosis	Range	Min	Max	Sum
4.3.a. Local facilities e.g. pub/tea shop	55	2.2	0.2	2.03[a]	1[d]	1.3	1.7	1.4	0.3	2.2	0.6	5.0	1	6	123
c. Wildlife and landscape	55	1.8	0.2	1.53[a]	1	1.2	1.5	1.8	0.3	3.5	0.6	5.0	1	6	98
d. Archaeology and history	55	2.7	0.2	2.55[a]	3	1.2	1.5	1.2	0.3	2.4	0.6	5.0	1	6	146
e. Location in the National Park	55	2.7	0.2	2.50[a]	3	1.5	2.1	1.2	0.3	0.9	0.6	5.0	1	6	150
Do you think Hebden Beck is important to the village?	55	1.3	0.1	1.16[a]	1	0.6	0.4	2.3	0.3	3.6	0.6	2.0	1	3	69
Why do you think Hebden Beck is important to the village of Hebden?															
a. Provides a wildlife habitat	55	1.9	0.2	1.40[a]	1	1.6	2.7	2.0	0.3	2.7	0.6	5.0	1	6	102
b. Provides an attractive focus for the village	55	2.0	0.2	1.57[a]	1	1.5	2.4	2.0	0.3	2.8	0.6	5.0	1	6	108
c. Supports farming & fisheries	55	2.3	0.2	1.79[a]	2	1.7	2.8	1.6	0.3	1.2	0.6	5.0	1	6	125
d. Supports other business sectors	55	2.7	0.2	2.27[a]	2	1.7	2.8	1.1	0.3	0.0	0.6	5.0	1	6	147
e. Source of drinking water	55	3.3	0.2	3.08[a]	3	1.6	2.6	0.5	0.3	-0.8	0.6	5.0	1	6	184
f. Attracts visitors to the village	55	2.0	0.2	1.50[a]	1	1.6	2.6	1.8	0.3	2.0	0.6	5.0	1	6	108
How would you rate the water quality in Hebden Beck?	55	2.7	0.2	2.24[a]	2	1.7	3.0	1.0	0.3	-0.3	0.6	5.0	1	6	150

Appendix 5.7 (continued). Outputs from statistical descriptive analysis in SPSS.

Visitors	N	Mean	Std. Error of Mean	Median	Mode	Std. Deviation	Variance	Skewness	Std. Error of Skewness	Kurtosis	Std. Error of Kurtosis	Range	Min	Max	Sum
Do you think that the water quality in Hebden Beck should be improved?	55	2.1	0.1	2.21[a]	3	0.8	0.7	-0.3	0.3	-1.6	0.6	2.0	1	3	118
Are you aware of national water quality standards for rivers/streams?	55	1.7	0.1	1.65[a]	2	0.7	0.4	0.4	0.3	-0.7	0.6	2.0	1	3	93
Are you aware of the lead mines around Hebden and their part in the local history of the area?	55	2.3	0.2	2.47[a]	1	1.4	2.1	0.3	0.3	-1.9	0.6	3.0	1	4	126
Do you think the mines have had any effect on the water quality of Hebden Beck?	55	3.6	0.3	3.37[a]	3	2.1	4.5	0.3	0.3	-1.1	0.6	6.0	1	7	198
Please tick the box which best corresponds to your opinion for each of the statements below.															
a. The mines discolour the water in Hebden Beck	55	2.3	0.1	2.36[a]	3	0.8	0.7	-0.6	0.3	-1.3	0.6	2.0	1	3	125
b. The moorland above the village discolours the water in Hebden Beck	55	1.4	0.1	1.28[a]	1	0.7	0.5	1.6	0.3	0.9	0.6	2.0	1	3	76
c. The mines discharge heavy metals into Hebden Beck	55	2.2	0.1	2.25[a]	3	0.9	0.8	-0.3	0.3	-1.8	0.6	2.0	1	3	119

Appendix 5.7 (continued). Outputs from statistical descriptive analysis in SPSS.

Visitors	N	Mean	Std. Error of Mean	Median	Mode	Std. Deviation	Variance	Skewness	Std. Error of Skewness	Kurtosis	Std. Error of Kurtosis	Range	Min	Max	Sum
d. Water from the mines only enters Hebden Beck after heavy rainfall	55	2.2	0.1	2.26[a]	3	1.0	0.9	-0.3	0.3	-1.9	0.6	2.0	1	3	119
e. Farming activities are affected by the mines	55	2.2	0.1	2.33[a]	3	0.9	0.8	-0.5	0.3	-1.6	0.6	2.0	1	3	123
Do you think that recent flooding events can affect the water quality of Hebden Beck?	55	1.3	0.1	1.17[a]	1	0.7	0.5	2.2	0.3	2.9	0.6	2.0	1	3	70
As the person completing this questionnaire, please indicate your age range:	55	3.7	0.2	3.84[a]	5	1.1	1.3	-0.7	0.3	0.0	0.6	4.0	1	5	206
As the person completing this questionnaire, please indicate your gender:	55	1.6	0.1	1.53[a]	1	0.6	0.4	0.7	0.3	-0.5	0.6	2.0	1	3	86
How would you describe the working status of your household?	55	2.0	0.2	1.68[a]	1	1.5	2.2	2.2	0.3	5.0	0.6	6.0	1	7	111
How often do you visit Hebden?	55	4.1	0.2	4.22[a]	4	1.4	2.0	-0.6	0.3	0.4	0.6	6.0	1	7	227

Appendix 5.7 (continued). Outputs from statistical descriptive analysis in SPSS.

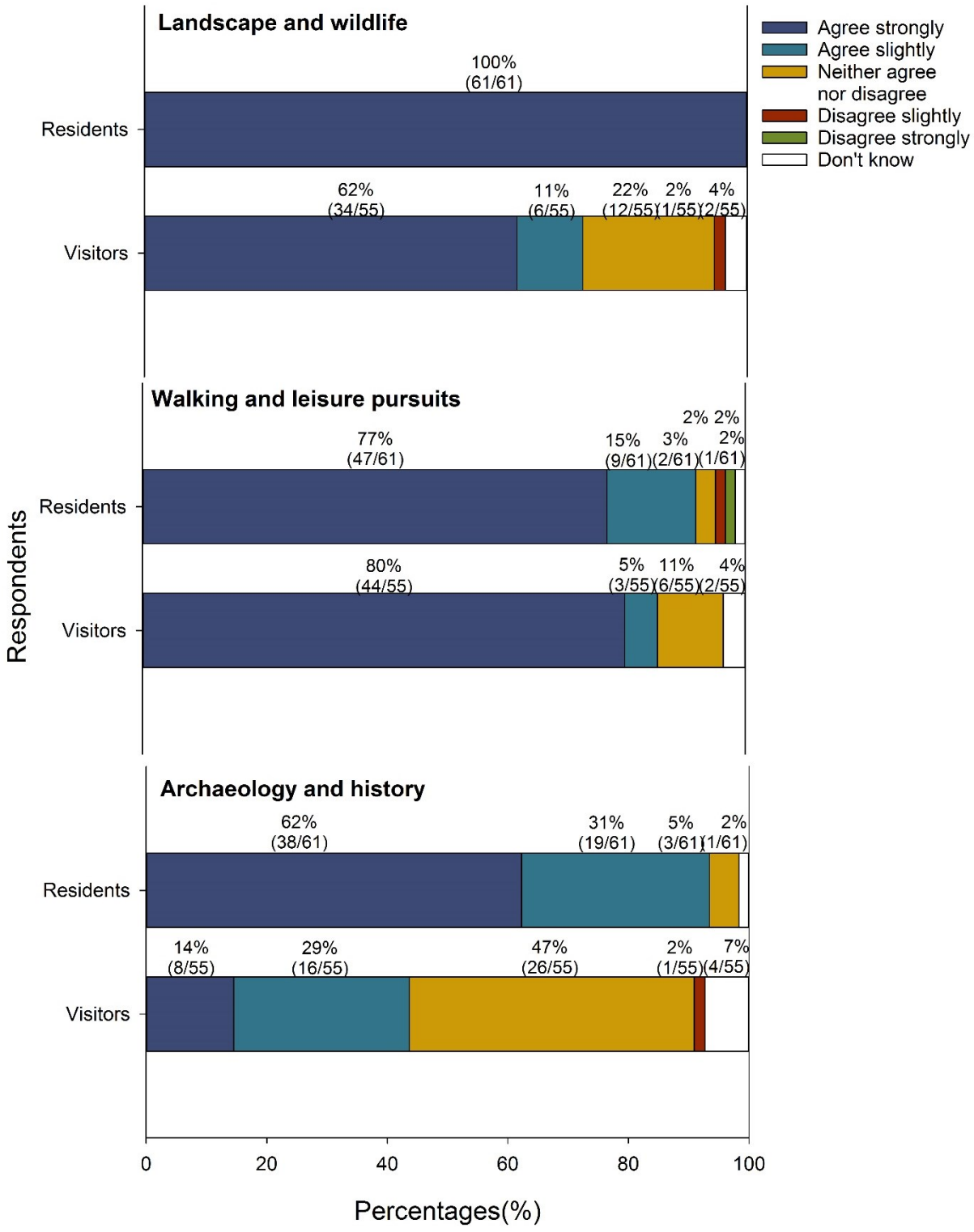
Stakeholders	N	Mean	Std. Error of Mean	Median	Mode	Std. Deviation	Variance	Skewness	Std. Error of Skewness	Kurtosis	Std. Error of Kurtosis	Range	Min	Max	Sum
How important do you think Hebden Beck is to the village of Hebden?															
a. Provides a wildlife habitat	5	1.8	0.2	1.80[a]	2	0.4	0.2	-2.2	0.9	5.0	2.0	1	1	2	9
b. Provides an attractive focus for the village	5	1.8	0.2	1.80[a]	2	0.4	0.2	-2.2	0.9	5.0	2.0	1	1	2	9
c. Supports farming & fisheries	5	1.8	0.2	1.80[a]	2	0.4	0.2	-2.2	0.9	5.0	2.0	1	1	2	9
d. Supports other business sectors	5	3.4	0.7	3.00[a]	3	1.5	2.3	1.7	0.9	3.7	2.0	4	2	6	17
e. Source of drinking water	5	4.0	0.6	4.00[a]	3	1.4	2.0	0.9	0.9	-1.8	2.0	3	3	6	20
f. Attracts visitors to the village	5	1.8	0.2	1.80[a]	2	0.4	0.2	-2.2	0.9	5.0	2.0	1	1	2	9
Are you familiar with the national water quality standards for rivers/streams?	5	1.2	0.2	1.20[a]	1	0.4	0.2	2.2	0.9	5.0	2.0	1	1	2	6
How would you rate the water quality in Hebden Beck?	5	5.6	0.2	5.6000[a]	6	0.5	0.3	-0.6	0.9	-3.3	2.0	1.0	5.0	6.0	28.0
Are you aware of the historical lead mines around Hebden?	5	1.4	0.4	1.40[a]	1	0.9	0.8	2.2	0.9	5.0	2.0	2	1	3	7
Do you think there is an environmental legacy of the lead mines in the area?	5	1.0	0.0	.[a]	1	0.0	0.0		0.9		2.0	0	1	1	5

Appendix 5.7 (continued). Outputs from statistical descriptive analysis in SPSS.

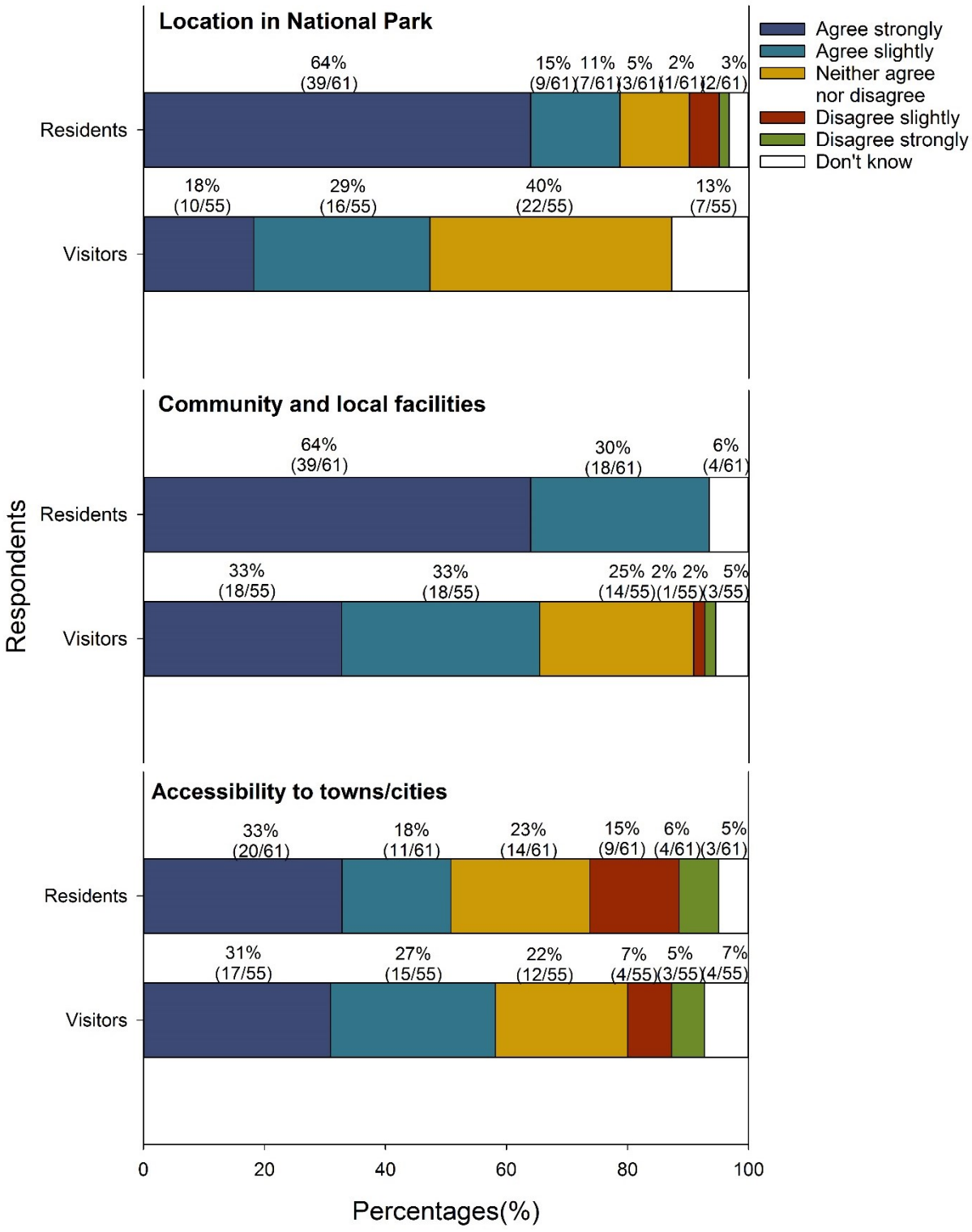
Stakeholders	N	Mean	Std. Error of Mean	Median	Mode	Std. Deviation	Variance	Skewness	Std. Error of Skewness	Kurtosis	Std. Error of Kurtosis	Range	Min	Max	Sum
Do you think the mines have or are influencing the water quality of the river?	5	1.4	0.4	1.40[a]	1	0.9	0.8	2.2	0.9	5.0	2.0	2	1	3	7
Do you think intense rainfall events may alter the influence of mine/mining wastes on the water quality of Hebden Beck?	5	1.4	0.4	1.40[a]	1	0.9	0.8	2.2	0.9	5.0	2.0	2	1	3	7
Do you think water quality in Hebden Beck can be improved without detracting from landscape/heritage?	5	1.8	0.5	1.8000[a]	1.00	1.1	1.200	0.6	0.9	-3.3	2.0	2.0	1.0	3.0	9.0

a. Calculated from grouped data.

d. *Multiple modes exist. The smallest value is shown.*



Appendix 5. 8. Perceptions from residents and visitors about the Hebden's main attractions.



Appendix 5. 9. Perceptions from residents and visitors about the Hebden's main attractions.

Appendix 5. 10. Interview transcript

Duration: 00:40:00
Date: 29/07/2016

Interviewer: Thank you for taking time to talk to us today.

Respondent: It's fine.

Interviewer: If any of my questions are unclear, please let me know.

Interviewer: How long have you live in the village [Hebden] roughly?

Respondent: I live just outside the village of Hebden Gill which is half a mile to the north and the family have been there about 300 years. But I've live here full time since 1967.

Interviewer: So, it is a considerable time.

Respondent: I'm almost local, yes.

Interviewer: So are you interested as well in the mining history?

Respondent: Yes, very much so.

Interviewer: Have you always had that interest?

Respondent: Yes, I think because my family, if you go way back, were farmer miners. They combined farming with mining, and I'm most into writing as my main occupation, writing and publishing and hence a strong interest in mining in particular in this valley and on Grassington Moor which is closely related.

Interviewer: Okay, so you know a great deal about the history of mining.

Respondent: Yes, a reasonable amount, I do.

Interviewer: So we were a bit confused over the two mines, you know the Yarnbury or Beaver, (someone else told us it is call Beaver) and then there is Grassington and then is Hebden.

Interviewer: So where Hebden mines are?

Respondent: Hebden mines are virtually alongside the beck, about three quarter of miles of the valley.

Interviewer: Okay, right so it is around Bolton Gill?

Respondent: Yes indeed, Bolton Gill was the heart of the Hebden mines.

Interviewer: OK.

Interviewer: Then beyond that you come into the Grassington fields which is far longer established, going way back to the early 1600, while Hebden was the 1850 towards the end of lead mine. It was a lead vein. Very profitable. Most of these villages in

particular the main street was re-built from the proceeds of lead mining of Hebden mines

Interviewer: Oh ok, so from the 1850 onwards?

Respondent: Yes, they only had a short live of about 10 years.

Interviewer: Oh ok…

Respondent: So it was not so much mining in getting everything out, take the profits and suddenly fails, because lead was the most unpredictable industry in terms of extracting it.

Interviewer: Yes you have to find the right vein, haven't you?

Respondent: Yes, it's luck, it's luck.

Interviewer: Have you went into them [mines], how is it?

Respondent: Yes, it's dark, dank, and gloomy.

Interviewer: Has it changed since then? Has it changed considerably, I mean is it safer?

Respondent: Not a lot. They were ruins then, there has been gradually declined in recently years. The other side of the coin it has been quite a lot of restoration, particularly on Grassington Moor where there is now a good visitor trail. In Hebden, this year has been some restoration of the buildings.

Interviewer: Ok, is that to make them safe?

Respondent: Yes, indeed to conserve them. Conservation that is all, which is good.

Interviewer: Did you say you were here in the 60s. So, they did re-processing of the Grassington spoils?

Respondent: They did, yes.

Interviewer: Did they built some extra buildings.

Respondent: Yes they built extra buildings, they took mains of electricity out there which in fact brought electricity to the outline farms on its way. That might have been the case but did cause some severe pollution problems to the extent that one year, the processing facilities broke down and all the fish in the beck were poisoned, well over a thousand of them, it was amazing. We've no idea there were some many trout.

Interviewer: So there are many trout in the river now?

Respondent: Yes, but you never see them. You can see them in a deep pool if you look down, but that [event] was a revelation as to just how many were in this beck and they had a significant size of about 30 cm.

Respondent: Well, I suspect you know all about the history of lead as a pollutant and it being very long term. Indeed there was deaths of cattle once at that stage in the 1950. I

think that again it was related to the re-processing of the mining slag heaps, stirring up the pollution of it.

Interviewer: OK

Respondent: It is interesting if you walk up the valley you will see slag heaps, spoils heaps. The last work was 30 years ago and not a blade of graze has grown on them yet.

Interviewer: Yes

Respondent: That is very noticeable. Lead is very serious.

Respondent: Going back to the 19th century lead is a very slow poison, proved by the death of people on the Franklin expedition to the North West Passage which is got down to lead poisoning in the food. I always feel that using lead for all the plumbing and pipes, in the village must made us rather a peculiar lot, probably it did.

Interviewer: But it was not just in the village with the lead pipes, it was wholesale in Victorian properties.

Respondent: We have a big local use of lead pipes, lead was also invaluable for roofing.

Interviewer: All the local lead probably still on the rooves.

Respondent: Yeah.

Interviewer: So, given what you just said about the reprocessing took place, do you think there is an environmental legacy of the mines even today?

Respondent: I don't think so. I think it has settled down, probably not you want me to tell you…

Interviewer: No, no. It's your opinion, that it's what we want.

Respondent: It has settled down, that is on the core, I mean coming into Hebden beck is Duke's level, which was the master [drain] for all the Grassington mines and that it's what is bringing in a certain amount of lead in it but when there was a severe drought was about in 1976 the water authorities were quite happy as temporary measure to take water from Duke's level.

Interviewer: Oh really, for drinking water?

Respondent: Yes. You still can see a big blue pipe near the level actually near the entrance of the level if you look closely which did they said the crisis there were a very severe drought. It helped a lot, they wouldn't have done that if they still had been considered a remote risk or so diluted that where no risk at all.

Interviewer: Is there a Lanshaw adit, reservoir?

Respondent: Yes, there is Lanshaw level is going into a small reservoir. The history of it again it was considered good water it was taken over to a Grassington Sanatorium considered a TB hospital (associated with treatment of tuberculosis) between Hebden and Grassington where the purity of the water must has been considered essential.

Interviewer: Right, do you know if that is still in use?

Interviewer: No, it's no used now.

Respondent: All the water around here now comes from a great circuit from Grimwith Reservoir (biggest reservoir) between here and Pateley Bridge.

Interviewer: It [Grimwith Reservoir] was quite low actually.

Respondent: The water authority will probably say that it [Grimwith Reservoir] is expected to be low.

Interviewer: Maybe it is the lowest time of year. Apart from the mines do you think there are other major causes of pollution to the river, other than the mines? Maybe farming activities?

Interviewer: Yes, well excess of uses of nitrates by farming today the usual allegation should I say. But they can be a certain amount runoff from farms including pasture lands particularly at the bottom of the valley, bottom of Hebden Gill close to the village but in what extent this is a problem I need an expert knowledge which I don't have.

Interviewer: Well you have live here and you have seen it over the years?

Respondent: Oh yeah, […], you see all this cycle from the traditional hay meadow, when I was a young boy the field were full of the most wonderful flowers but then farmers had to be paid to improve them and now they are paid to make them tripled their sizes [but also] to conserve them, so the wheel has come full circle. At an initial cost with the use of nitrates and so on, but in a way that I suspect that has declined because we are now in an environmental sensitive area with all the restrictions that are up to now applied, I say up to now because of Brexit (we don't know what is next…)

Interviewer: Have you notice a difference of the observable quality of the water, over the years...

Respondent: No I can't say over the years. But I have noticed how the colour of it has changed, but that is down particularly after a dry period when certainly get rain and the water coming out from moor which are peat so the water simply goes brown because of that.

Another controversial one has been gripping as we call it and that is draining of the moors for improving for shooting. Again that have come full circle, because in some cases there are now grants to eliminate the gripping, so do go around in circles. But certainly that creates more rapid runoff and that is way in my youth the moor were as a sponge they absorbed the water in a way they now don't, it comes down much more quickly hence the beck has gone down by the time you get here from Leeds in some cases.

Interviewer: Yes we have noticed that it is incredible responsive, it really is…

Interviewer: Flooding as well have you noticed an increase in water heights quantity?

Respondent: Yes, yes we do. I mean it is all connected, climate change what extent it is there or is not but certainly we are more prone to flash flood that it used to be the case we are tend to be getting one about every couple of years now.

Interviewer: Ok, but it is in the same place along the beck or is in different places?

Respondent: No it is interesting. They can be extremely local storms. As I said we live half a mile from here and you hear the beck when there is an extreme flood. We were mystified about 18 months ago when there was an extreme flood where we did not have a drop of rain, that was because of the flush from a thunderstorm further up the valley. Actually quite enough to cause a ground disturbance. Because if you go north from here you have one [hill]side which in my language is 200 or 300 feet high and therefore storms can […] against it with spectacular results.

Then we had normal flow due to moor side spread, certain rainfall that all [running off], it is called the valley problem. For example, certainly it is not confined to the Calder valley, it just suffers because it is so narrow.

Interviewer: So you are getting this massive events, storm events.

Respondent: Yes, but nothing to cause damage to buildings and properties in Hebden. Which I think the wise builders of those days due to build where they were not at risk basically.

Interviewer: It seems that they are sensible located, that is reassuring.

Respondent: Referring to your questionnaire (no quoting exactly).What influence has the beck on the village or how much it is appreciated? Probably rather it is taken for granted these days. It is there, attracts the visitors because it is attractive further up. But not hugely important in the sense that it used to be if you go a way back in history to power water wheels and all that sort of things.

Interviewer: and for drinking water extraction?

Respondent: Well I presumed so I have never be able to establish that. I just suspect that people knowing that lead mining has been going on for 400 years they would not drink from the beck. Since certainly in this village there are counts of water laboratories been bucketed from the spring across so they are aware not to drink it. Because they will be right enough to know some suddenly illness could be related to water.

Interviewer: Well, lead has long been recognised as a poison.

Respondent: Yes indeed, time was in the 19th century that they got very sensitive for water borne illnesses like typhoid and so on they were gradually careful with what they did.

Interviewer: So now I will ask you some questions as well about the existing management of the river, you have mentioned that you have spoken with the EA?

Respondent: Yeah, informally when I have seeing them doing the monitoring.

Interviewer: Are there any other agency, individuals, or companies that have you spoken about water related issues?

Respondent: No, the water that is measured by the water authority rather than EA that rated flow but that will be related to safeguard angling interests further down, I just don't know as a general package but I don't have contact with them. Well, I think in a regular basis the EA comes to check pollution levels but that it is about it, otherwise the water just flows.

Interviewer: Do you think people in Hebden are aware that the Environment Agency comes and does this monitoring?

Respondent: I think people are aware of everything [the EA is doing]. But providing it [the monitoring and assessment] doesn't mean that you are involving them [residents] directly, well they [residents] would say, it's happening, it's not to do with us.

Interviewer: I just wonder whether if you would be more interested to know more about their results?

Respondent: Yeah, I would be [interested in the EA findings]. Because now it [the EA data, has] just disappeared into a black hole as far I'm concerned. It will be nice to have a summary about what they are finding and why they are doing it. As similar with the parish council, presenting something not in a weekly or monthly basis just once a year about what they are finding and how trends are changing. That it will be very good.

Interviewer: Thanks this it is what we want to find, what people do want to know...

Respondent: Yeah, I don't think the Environment Agency is deliberately being secretive. They are just getting on with their job but not considering that what they are doing will have a local interest.

Interviewer: Here is where the university could help.

Respondent: Yes, I'm sure it can.

Interviewer: So did you mention the parish council and possible sending information to them, is there any another mechanisms that we could maybe engage with the community?

Respondent: I'm biased I should say. Because I'm an active member of the Parish council, I should say that in fairness to give you a general picture. The parish council does really distribute information to the village, there is an annual newsletter on everything that is happening in the village, which try to be fairly up to date, and get it to people by modern means or traditional means. They have an annual meeting with everybody living in the village. Parish council is really the avenue to receive information. They can receive it electronically so that would be good if it can be done.

Interviewer: So this annual meeting involving all the village, is it well attended?

Respondent: Well about 15% of the residents.

Interviewer: How many people are real residents?

Respondent: Well, about 250 residents. Hebden has better percent [of residents] than other villages. We are still a working farming community, which is good. But we cannot do nothing about secondary homes, it is part of 20th century development. But as community Hebden Beck is still here.

Interviewer: With your interest in the mines have you find a lot of interest from the local people?

Respondent: Yes, local people from Grassington, they were fascinated by the mining characters because is something unusual with lead mining been confined to relatively few areas in the country.

Interviewer: So the lead mines are the reason because Hebden is here?

Respondent: No, most of the villages that have lead mining, farming came first for a 1000 years, there are still farmers in the village that have been farming 400 years ago. To find mine villages you have to head west up to the hill to Greenhow on the top between here and Pateley Bridge.

Respondent: Hebden is a farming village that did briefly mining and benefited from it.

Interviewer: How would you feel about some management solutions involving doing something with the spoils?

Respondent: My opinion might be different to that advising about ancient monument. But it is a matter of how archaeology it is perceived as a matter of health risk.

Interviewer: But do you thing the spoil heaps are important to the area?

Respondent: No, but I think some of the buildings are historical hugely important (e.g. Bolton Gill level, Duke's level). But spoil heaps are heaps to spoil.

Interviewer: Thank you so much for your time and important inputs to this research.

References of Appendices

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